MECHANISMS OF MULTIPLE INFRARED PHOTON
ABSORPTION AND DISSOCIATION

by

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MECHANISMS OF MULTIPLE INFRARED PHOTON
ABSORPTION AND DISSOCIATION

by

Christopher Reiser

Submitted to the Department of Chemistry
on May 23, 1980 in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

ABSTRACT

The infrared laser induced multiple photon reactions of olefins of the type R₂C=CHCl have been investigated. In all cases, the dominant mode of reaction is elimination of HCl, although free rotation around the double bond may precede elimination. Clear evidence for the formation of the vinylidene carbene F₂C=C: from F₂C=CHCl was shown although the case for the corresponding dimethyl species (CH₃)₂C=C: is not as convincing. The experimental results for the vinyl chloride system can be represented with a kinetic model with rates calculated from RRKM theory, which assumes an unhindered flow of energy amongst the vibrational modes prior to reaction.

Spectroscopic studies of species undergoing multiple infrared photon absorption was begun with infrared laser double resonance spectroscopy in the ν₁ band of SF₆, using a CO₂ laser pump and a tunable diode laser probe. Effects of saturation and dynamic Stark shifting are clearly seen in 2-level and folded 3-level spectra. No mixings via the molecular vibration-rotation Hamiltonian sufficiently strong to influence the spectra were found. K-changing collisions were invoked to explain the apparent disparity between the observed spectra and the spectra predicted from lineshape theories derived from 2-level and 3-level Bloch equations. From the decay of the double resonance signals, we measured relaxation times \( T_1 = 24±3 \) nsec·Torr for 2-level signals and \( T_1 = 43±11 \) nsec·Torr for 3-level signals.

Thesis Supervisor: Dr. Jeffrey I. Steinfeld

Title: Professor of Chemistry
To my family and to Libby
PREFACE

Since most of this work has been word-processed on a MINC computer, some stylistic conventions have been adopted to accommodate the LA34 DECW RITER IV printer. This device is not capable of typing subscripts, superscripts or Greek symbols; where appropriate, these symbols have been inserted after the printing of the manuscript by the computer. References have been denoted in the text not as superscripts but as a number enclosed in square brackets, e. g. [X.Y], where X is the Chapter (or Appendix) identifier and Y indexes references within each chapter. In all other matters, the guidelines outlined in the MIT Archives booklet, "Specifications for Thesis Preparation" (1979) have been observed.
ACKNOWLEDGMENTS

Many members of the Basement Executive Council deserve my thanks for lasting friendship and tutoring. B. D. Green first taught me to align a laser; Fran Lussier introduced me to the joys of DeKhotinskii cement. Craig Jensen deserves special mention as a fast friend who provided stimulation in many areas of chemistry; he remains the only man in my memory whose callouses cannot be shown in public. Long nights were spent slaving over DILDOR with Tom Anderson, who renewed my interest in drinking after the departure of C. Jensen. Other Council members must be acknowledged for stimulating discussions, including Tom Quelly (the skies are safe), Jim Long (still finding a tube with no hole), Mark "Maypo" Spencer, Bobbi Roop and Dave Harradine. Joe Francisco merits honorable mention as the most difficult case I have yet encountered in a Chinaman.

Other basement rats should also be noted; Ed Murphy, for one, always provided timely excuses for adjourning to the Muddy. I am indebted to Mike McClellan, Rick Gottscho and my ex-roomies Lou Nucci, Gary Hattery, Steve "Gobble" Koch and Jeff de Roulet for muchly appreciated comaraderie. My best wishes go to Graham Arnold.

Of the faculty, my advisor Jeff Steinfeld deserves my deep gratitude for his generous support and continuously challenging banter. While it is not true that we have stolen his key to the lab, we have found that independent thinking is of paramount importance in practical situations. Bob Field the Boy Wonder came to my aid many times, and I hope he never forecloses on the FF100 I may still owe him. F. "Bombay
Slums" Read McFeely, Purveyor of Pandemonium and Keeper of the Screw, deserves anything he gets. Bob Silbey, on the other hand, has escaped capital punishment only by disguising himself as a theoretical professor; in reality he is the great-great-great grandfather of the Klingon race.

Special thanks go to Vera Spanos for shelter from the madness, to Raphie Levine for a very pleasant ascent of Pike's Peak, and to Libby Huggins for keeping me sane.

I am indebted to Will Gilbert of Prof. Petsko's group for taking the time to print the final version of this work on the line printer of their PDP 11/60 computer system.
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Chapter 1. Background

Although photochemistry has been actively studied for many decades, the advent of continuously improving laser technology has caused a renaissance of interest in the use of light in chemistry. A particular laser induced process may take advantage of any of the various properties unique to laser radiation, such as high spectral intensity, narrow linewidth, short pulse duration or facile beam directability. Applications have ranged from gross laser heating and pyrolysis, such as in thermal diffusion columns [1.1] or the production of sinterable powders [1.2], to state-selective excitations, such as vibrational energy enhancement of the bimolecular HCl + K reaction rate [1.3].

Laser induced and laser enhanced chemistry has blossomed in the past several years into a full-scale discipline whose central theme is influencing chemical events by coupling energy, via laser radiation, into the various molecular degrees of freedom. The discipline is so broad that we must restrict our scrutiny from the start to a small subset of laser induced chemical processes. In this thesis, this subtopic involves the intimate chemical and physical processes incurred in the megawatt infrared laser induced dissociation of small molecules.
Multiple infrared photon absorption (MIRPA) is a relatively new area of research. The first observation of MIRPA may be ascribed to Isenor et al. [1,4], who employed a CO₂ TEA laser to irradiate low pressure samples of SiF₄, NH₃ and other molecules at intensities of up to 10⁹ W/cm². Visible fluorescence emitted from the samples was attributed to emission from highly excited parent molecules or photofragments. The authors' interpretation stated that sufficient energy was absorbed into the near resonant molecular vibrations to cause direct collisionless dissociation, since the emission followed the 200 ns laser pulse in temporal and geometric shape. Absorption of multiple photons presumably occurred through a series of discrete overtone vibrational states until the density of vibrational states, or number of vibrational states per unit energy, became a "quasi-continuum", thus providing a facile pathway for the absorption of energy from the laser field. In this manner, the absorption of 20-40 photons was envisioned.

Within the next several years, Ambartzumian et al. [1,5] and Lyman et al. [1,6] reported isotopically selective laser induced dissociations of SF₆. In these experiments, gas samples of SF₆ with a natural abundance of sulfur isotopes were enriched in either ³²S or ³⁴S. The enriched isotope could be chosen by tuning the CO₂ TEA laser used to irradiate the samples to the J₃ band frequency of the unwanted isotope, thereby preferentially dissociating unwanted isotopic molecules. The large ³J₃ dipole moment, high
isotopic shift of the $\nu_2$ fundamental frequency, coincidence with CO$_2$ laser frequencies and spectroscopic similarity to UF$_6$ made SF$_6$ an "ideal" candidate for studying MIRPA and laser induced dissociation (LID).

In his dissertation, Jensen [1.7] gives a sweeping tour of the experiments and interpretations of the MIRPA process in SF$_6$. This process is not restricted to hexafluorides, but in fact has become a general process occurring in a wide range of molecular sizes and types [1.8]. Several recent review articles attest to the popularity of the field [1.9] and provide specific details for the interested reader.

Usually LID experiments are carried out at pressures ranging from a few microns to tens of Torrs of parent molecules. In some cases, inert or scavenger buffer gas may be added. To achieve the intensities required to force MIRPA to occur, the TEA laser output is focused into the sample cell so that peak intensities fall in the $10^6$ to $10^9$ W/cm$^2$ range. The net chemistry is inferred, after a suitable number of laser pulses, by IR spectrophotometry, gas chromatography, mass spectrometry and other means. In some cases [1.10] in situ analysis techniques have been employed to determine the identity of the primary photofragments. For the most part, however, the photochemist has been left the often tedious chore of determining the primary photochemistry from the net chemical products.
The value of the MIRPA approach to photochemical reactions lies ultimately in the ability to choose what the primary fragments will be. Initially it was hoped [1.11] that mode specific chemistry could be achieved, wherein reactions involving specific bonds could be forced by exciting appropriate vibrational modes. This would be a "chemist's dream", that is, to obtain the ability to perform a specific reaction seemingly at will. As we shall see in Chapters 2 and 3, however, the criteria necessary to achieve mode selective behavior appear to be particularly elusive in the laboratory. Lack of mode selectivity or specificity does not imply uselessness, however. As mentioned above, isotopic enrichment continues to be a major application of megawatt infrared photolysis; isotopes of C, H, S, Cl, and B have been separated, just to name a few. Creation by LID of high local densities of exotic species has been used by King and Stephenson [1.12] in their spectroscopic studies of CF$_2$. In a similar manner, Steinfeld et. al. [1.13] used high local concentrations of reactive radicals produced by LID to etch an SiO$_2$ surface placed close to (but not in) the TEA laser beam. Although no LID process has actually been applied in a commercial enterprise, the projected cost of some LID processes, such as deuterium enrichment, have begun to approach the cost effectiveness of currently used techniques [1.14]. Perhaps the greatest stumbling block to further
applications of LID is a lack of understanding of the rates and mechanisms of fundamental physical processes which contribute in concert to the observed net chemistry. Only a limited understanding of the intimate details of the dynamical process can be had from analysis of chemical evidence after the event is completed. Despite a growing mass of elegant experimental evidence, large gaps in our understanding still exist. Specifically, experimental efforts should be aimed at four interleaved questions:

1) How does a molecule absorb multiple photons? This question cannot be answered by bulk chemical methods. It requires a detailed understanding of the interaction of very intense infrared fields with molecules having near resonant vibrational modes. Spectroscopic parameters specific to each example molecule must play an important role, so that effects of sample pressure, laser frequency and laser intensity (or fluence) are adequately describable.

2) How does the vibrational energy distribute in the molecule? Once energy has been absorbed, collisional or spontaneous intramolecular energy relaxation will tend to distribute energy in modes other than the mode which was originally resonant. The speed of intramolecular vibrational relaxation (IUR) is evidenced in many LID experiments, for example (1.15) in the LID of CF$_3$Br,

\[
\text{CF}_3\text{Br} \xrightarrow{\text{nh}_j} \text{CF}_3 + \text{Br} \quad (1-1)
\]
energy is placed initially in CF stretches although it is the bromine bond which breaks. Presumably the speed and extent of IUR influences the chances of observing mode specific chemical behavior and of using models of unimolecular reaction rates based on a statistical distribution of energy amongst the vibrational modes, such as the RRKM method (1.16).

3) What kinds of exotic reactions can be expected? To answer this question we must understand how laser excitation differs from simple heating (which is the key to question (2)) and what unimolecular kinetics the molecules follow given that excitation. Since using a laser to produce chemistry that can be done by more conventional techniques is at best uneconomical (1.14), reaction mechanisms unique to this form of excitation must be elucidated before LID can find significant applications in experimental and commercial technology.

4) Can a simple model be used to predict LID phenomena? Presumably once a reasonably complete set of absorption, relaxation and reaction rates are known for a particular system, a sufficiently large computer code could model the system behavior. In many cases, however, the ability to predict chemical behavior with a simpler, analytical model would be of greater use in applying MIRPA to a particular chemical problem.

The experimental approach we have used over the past several years has been designed to illuminate various portions
of the complex set of problems outlined above. In many cases the work done in our laboratory has complemented that done elsewhere, and the combination of experimental results has greatly improved the scope of our understanding. Thus our work, and the work reported in this thesis, does not comprise an exhaustive series of experiments on the subjects involved in MIRPA, but has been chosen as our knowledge progressed to attack a few key points where our understanding of the LID process was particularly thin.

Originally the data collected were chemical in nature, aimed at answering question (3) above. F. M. Lussier [1.17] initiated work on the infrared photolysis of vinyl chloride, which was considerably extended to include a host of halogenated olefins. This work is contained in Chapters 2 and 3 and in Appendices A, B and C.

Net LID chemistry of the type described in Appendix A showed what experimental parameters play significant roles in influencing various stages of the LID process. Sample pressure, laser beam geometry, pulse intensity or fluence and other more subtle factors were found to influence greatly the total amount of energy deposited in the molecules. The simple kinetic schemes we used to model our LID results in the vinyl chloride system showed that the average energy absorbed per molecule \( \langle E \rangle \) is strongly dependent on experimental conditions such as initial gas sample pressure, the presence of cold diluents which tend to deactivate excited molecules,
and beam geometry (which we review in Chapter 4 and Appendix D).

When a model for a LID process is constructed, a reliable estimate of the internal energy-dependent reaction rates much be obtained. In all kinetic models of LID with which the author is familiar, RRKM unimolecular reaction rate theory [1.16] has been used to describe the microscopic rates of reaction quantitatively. The success of the RRKM method in modeling dissociation rates over a wide variety of LID conditions and reactions (such as isomerization, cyclic molecular elimination and simple bond scission) has been remarkable. The implications of the success of RRKM rates for answering question (2) above will be discussed in Chapters 3 and 7.

One question which has not been resolved experimentally involves the quantitative observation of the distribution of molecules over energy created by MIRPA. Theoretical [1.18] and semi-empirical [1.19,1.20] models have "predicted" various distributions which in turn "predict" a variety of experimental data, but to date no direct measurement of a MIRPA distribution has been made. As Jensen [1.7] pointed out, a distribution is not uniquely determined by chemical evidence alone. Direct observation, involving interrogation of individual species undergoing MIRPA, is necessary for direct comparison with existing dynamical theories.
Spectroscopic investigations of this nature have proven to be difficult to carry out. In molecules possessing no easily accessible excited electronic state, the lack of resonant excitation makes the usefulness of visible probe radiation very limited. We have chosen to use a tunable infrared diode laser to probe the vibrational bands themselves as they are being pumped by intense CO$_2$ laser fields. This work, Diode Infrared Laser Double Resonance (DILDOR), was begun by Jensen several years ago; in his thesis [1.7] he reported preliminary results in SF$_6$. Since that time our efforts at answering question (1), how SF$_6$ molecules interact with very intense resonant infrared fields, have been considerably extended, being included in Chapters 5 and 6 and in Appendix E.

In the DILDOR experiments accomplished thus far, the effects of power broadening, saturation, dynamic Stark shifting and collisional rotational relaxation have been studied in SF$_6$ for pump intensities up to $11 \text{ kW/cm}^2$. The limit of pump laser intensity and temporal resolution of the observed signals has been reached for the Q-switched laser pulses used in the currently existing apparatus. Moulton and Mooradian [1.21] have extended this work in SF$_6$ to higher pulse intensities but not to other molecules. A high repetition rate CO$_2$ TEA laser currently being constructed by Dave Harradine will enable these experiments to be extended to the intensities generally required for LID. The shorter length of the TEA laser pulse may also be valuable in studies
of collisional deactivation. Further improvements in the existing apparatus will be discussed in Chapter 6.
Chapter 2. Laser Induced Chemistry: Results

2.1 Introduction

As was pointed out in Chapter 1, a detailed understanding of the multiple infrared photon absorption (MIRPA) process necessitates interrogation of individual molecules. The gross behavior of an ensemble of molecules can then be "predicted" by a suitable average over the microscopic behavior obtained by these interrogations. Often, however, the experimentalist is faced with the reverse problem, that is, having information about an ensemble without knowing microscopic details. This is currently the case in the understanding of MIRPA and the chemistry it produces.

The clever chemist can, however, recover certain details of the microscopic dynamics of multiple infrared photon laser induced dissociations (LID) by using the chemical behavior of molecules as his method of interrogation. In chemical systems whose internal energy dependent reaction rates are well characterized, the known microscopic rates of dissociation become a valuable internal "yardstick" of internal energy content. By comparing the observed rates of reaction to the microscopic rates of reaction, the chemist can begin to make quantitative statements about the MIRPA process.

We have used this technique to study the LID of halogenated ethylenes, \( \text{X-CH-C=CH-Y} \) with \( \text{X = H, H, D, H, Cl, Cl} \) and \( \text{Y = H, D, H, Cl, H, Cl} \).
The report of these experiments has been published (J. Am. Chem. Soc. 101, 350 (1979)) and is included in this thesis as Appendix A. The reader is encouraged to peruse Appendix A before reading this chapter, so that he may be familiarized with the experimental method and results of the photolyses reported therein. The remainder of this chapter is devoted to experimental results not specifically reported in Appendix A but which nevertheless have aided our understanding of the MIRPA process and laser induced chemical reactions.

Some of the chemistry noted below has been published in a short note, included as Appendix B. The abbreviated account of the method of synthesizing the isotopically labelled molecules CHDCHCl and CH₂CDCl found in Appendix A has been expanded into much greater detail in Appendix C.

2.2 Kinetic model for CH₂CDCl

In Appendix A, the LID of CH₂CDCl was reported. The percent of $\delta,\delta$ elimination of HCl versus $\delta,\beta$ elimination of HCl was determined by GC/MS analysis of the acetylenes C₂HD and C₂H₂ produced. These data are reproduced in Fig. 2-1b.

Although it was claimed in Appendix A that these data are consistent with the RRKM picture presented for the more complicated system CHDCHCl, the details were not presented. For completeness, they will be included here.

The kinetic model for CH₂CDCl is similar to that used for
CHDCHCl and is constrained by the same assumptions as those put forth in Appendix A to qualify the use of this approach. In this case, the model is somewhat simpler, because isomerization need not be considered. Only two reactions occur,

\[
\begin{align*}
\text{CH}_2\text{CDCl} & \overset{k_1}{\longrightarrow} \text{C}_2\text{H}_2 + \text{DCl} \quad (78\%) \\
& \overset{k_2}{\longrightarrow} \text{C}_2\text{HD} + \text{HCl} \quad (32\%)
\end{align*}
\]

where

\[
\begin{align*}
k_1 &= k_{\text{gem}} \\
k_2 &= k_{\text{cis}} + k_{\text{trans}} = k_{\text{cis}}
\end{align*}
\]

In this model, trans elimination has been neglected, as in the model for CHDCHCl.

Using Eqns. (2-1), one can write immediately

\[
\begin{align*}
dA/dt &= -[k_1^I + k_2^I]A \\
d[C_2H_2]/dt &= k_1^I A \\
d[C_2HD]/dt &= k_2^I A
\end{align*}
\]

where \( A \) is convenient notation for \([\text{CH}_2\text{CDCl}]\) and

\[
\begin{align*}
k_1^I &= f k_1; \quad f = 5 \times 10^{-5}
\end{align*}
\]

The constant \( f \) is the approximate ratio of the volume interacting with the laser to the total volume of the reaction cell. Variations of \(-50\%\) of \( f \) change the net results by only 1 or 2\%.
Equations (2-3) and (2-4) can be integrated, using the boundary conditions of unit concentration of \( A \) and null concentration of acetylenes at \( t=0 \):

\[
A(t) = A(0) \exp(-[k'_1 + k'_2]t) \tag{2-6}
\]

\[
[C_2H_2](t) = k_1 A(0) [1 - \exp(-[k'_1 + k'_2]t)]/k_1 + k_2 \tag{2-7}
\]

\[
[C_2HD](t) = k_2 [C_2H_2](t)/k_1
\]

To find \( XC_2HD \), Equations (2-7) need be evaluated at some appropriate time, taken to be \( 10^{-7} \) reaction-seconds/pulse \( \times \) 1500 pulses = 150 microseconds, as is done in Appendix A.

The constants \( k'_1 \) must be calculated from the RRKM microscopic reaction rates, \( k^{RRKM}(E) \), by the same formula as prescribed in Equations (16)-(21) of Appendix A. These equations calculate the ensemble-averaged dissociation rates for two ensembles of molecules, one having a Poisson distribution \( f(E) \) of molecules over energy and the other having a maximum entropy distribution. Constants used in the calculation of the \( k^{RRKM}(E) \) are listed in Table 2-1.

The results of using Equations (2-7) are shown in Fig. 2-1 for energies of activation \( E_a \) identical to those which produced best results for the \( \text{CHDCHCl} \) system. For the maximum entropy distribution, a slightly different set of \( E_a \) renders a far superior fit. These adjustments are not much larger than the 1-2 Kcal/mole uncertainties of the values for the \( E_a \). This point will be discussed in the next chapter; for
Table 2-1. Vibrational frequencies of CH₂CDCl and transition state configurations (cm⁻¹).

<table>
<thead>
<tr>
<th>modeᵃ</th>
<th>molecule</th>
<th>ϕ-elim.</th>
<th>ψ-elim.</th>
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<td>(a')</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2305</td>
<td>2250</td>
<td>2200</td>
</tr>
<tr>
<td>2</td>
<td>3125</td>
<td>3100</td>
<td>3100</td>
</tr>
<tr>
<td>3</td>
<td>3030</td>
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<td>1595</td>
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</tr>
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</tr>
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<td>911</td>
<td>900</td>
<td>860</td>
</tr>
<tr>
<td>7</td>
<td>1110</td>
<td>7.50</td>
<td>r.c.</td>
</tr>
<tr>
<td>8</td>
<td>710</td>
<td>r.c.</td>
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</tr>
<tr>
<td>9</td>
<td>394</td>
<td>290</td>
<td>280</td>
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<tr>
<td>(a'')</td>
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<td></td>
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</tr>
<tr>
<td>10</td>
<td>805</td>
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</tr>
<tr>
<td>12</td>
<td>590</td>
<td>590</td>
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</table>

ᵃ listed in accordance with standard assignment; see Ref. [2.1] and [2.2]

r.c. = reaction coordinate
Figure 2-1. Effective branching ratios for HCl/DC1 elimination in the LID of CH₂CDCl. a) observed; ■ = P(38) laser line, △ = P(32). b) calculated; ○ = Poisson distribution with $E_a = 70$ and 69; △ = maximum entropy distribution with $E_a = 69$ and 73; † = maximum entropy distribution with $E_a = 70$ and 69 Kcal/mole for cis- and gem-elimination respectively. Solid curve drawn in a) has been included in b) for comparison.
### Table 2-2. Summary of LID experiments on isocrotyl chloride.

<table>
<thead>
<tr>
<th>Date</th>
<th>Notebook</th>
<th>p(I)</th>
<th>p(buffer)</th>
<th># shots</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/10/78</td>
<td>5W</td>
<td>0</td>
<td>4.8 MeOH</td>
<td>1500</td>
<td>P(16)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>only product in IR spectrum = C₂H₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/11</td>
<td>5Y</td>
<td>4.2</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>many peaks--some impurities</td>
</tr>
<tr>
<td>10/12</td>
<td>6Y</td>
<td>1</td>
<td>10 MeOH</td>
<td>1300</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>acetylenes formed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/13</td>
<td>7Y</td>
<td>5</td>
<td>22.1 H₂O</td>
<td>1500</td>
<td>no reaction</td>
</tr>
<tr>
<td>10/16</td>
<td>8W</td>
<td>0</td>
<td>32.3 NH₃</td>
<td>500</td>
<td>P(18)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>no changes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>white soot; great attenuation;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>very slight fluorescence</td>
</tr>
<tr>
<td>10/18</td>
<td></td>
<td>9.4</td>
<td>0</td>
<td>2500</td>
<td>submitted for GCMS analysis</td>
</tr>
<tr>
<td>10/30</td>
<td>9Y</td>
<td>3.2</td>
<td>29.8 H₂S</td>
<td>1500</td>
<td>IR weak; GC looks like blast of II alone</td>
</tr>
<tr>
<td>11/6</td>
<td>11W</td>
<td>4.9</td>
<td>48.3 H₂S</td>
<td>1500</td>
<td>same as last entry</td>
</tr>
<tr>
<td>11/7</td>
<td>11Y</td>
<td>8.6</td>
<td>13.9 H₂S</td>
<td>121</td>
<td>brilliant flashes; white soot; new</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>peaks in IR plainly seen</td>
</tr>
<tr>
<td>3/8/79</td>
<td>25Y</td>
<td>4.25</td>
<td>14.4 D₂S</td>
<td>1500</td>
<td>no fluorescence; for GCMS analysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remarks: P(16) = 9.6 p
Table 2-3. Summary of products seen in the infrared photolysis of isocrotyl chloride.

<table>
<thead>
<tr>
<th>GC peak #</th>
<th>rel. strength</th>
<th>ident.</th>
<th>Reasoning</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>allene</td>
<td>boiling point is lowest; mass peak 19.5 is unique to allene*</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>1,3-butadiene</td>
<td>mass peak 39 is very strong*</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>butadiyne plus 1-butyne or 1,2-butadiene</td>
<td>butadiyne is indicated by strong mass peak at 50; others must be included to account for a large mass peak at 54; bp's are very close for all three</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>2-butyne</td>
<td>bp is highest of those listed here; MS agrees with library</td>
</tr>
</tbody>
</table>

*library MS data have been taken from "Eight Peak Index of Mass Spectra" 1st ed., Vol. 1 and 2 (Mass Spectrometry Data Centre, Reading, 1970)
now we need to conclude only that the agreement between the observed and calculated points can be very good for either distribution $f(E)$. As was found in the CHDCHCl system, the mean energy $\langle E \rangle$ required to fit the data with the Poisson distribution is considerably higher than the $\langle E \rangle$ needed for the maximum entropy distribution.

2.3 LID of other halogenated olefins

2.3.2 Isocrotyl chloride, $(\text{CH}_3)_2\text{C}=\text{CHCl}$

The large fraction of gem elimination seen in the vinyl chloride system suggests that a radical of the type $R_2\text{C}=\text{C}$: may be formed. In the vinyl chloride system, reaction products that one would expect from this species were never detected, presumably because hydrogen migration occurs much too quickly. If the groups on the $\beta$ carbon were inhibited from migrating, however, the proposed intermediate might possess a sufficiently long lifetime to form bimolecular reaction products with added buffer gases. For this reason, the infrared photolysis of two additional molecules, 1-chloro-2-methyl propene (isocrotyl chloride, I) and 1,1-difluoro-2-chloroethene (II) was investigated.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{CH}_3\overset{\text{C}}{\text{C}}=\text{C}\overset{\text{Cl}}{\text{C}} & \quad \overset{\text{F}}{\text{C}}=\overset{\text{F}}{\text{C}}\overset{\text{Cl}}{\text{C}}
\end{align*}
\]

For the photolysis of I, a single Ge 11.1" (28 cm) focal length lens was used to focus the TEA laser beam into a 50 cm
Pyrex cell. The cell was fitted with a removable cold finger with a stopcock, a sidearm for cooling with LN$_2$ and a gas inlet for in situ evacuation and filling. For a typical run, the cell was filled to the desired pressure of I, which was then frozen into the removable cold finger and the stopcock closed. A known pressure of buffer gas was then admitted to the cell. The buffer gas and isocrotyl chloride was cryopumped into the sidearm. In this manner, mixing of the two gases was assured upon sublimation from the sidearm into the cell.

A summary of infrared photolyses done on the isocrotyl chloride system is shown in Table 2-2. Some difficulty was encountered during GC analysis of the reaction products; apparently certain GC columns reacted with the starting materials. From the IR spectra and GCMS results, however, it was determined that the reaction products of photolyses with added buffer gases did not differ significantly from photolyses with no buffer gas. Particularly significant is the lack of deuterium in the MS of products formed in photolyses with D$_2$S as the buffer gas.

Products that were formed comprise a host of C4 hydrocarbons. Although the cracking patterns of many of these olefins and alkynes are very similar, the GC peaks can be ordered by boiling point and elemental composition assigned by the mass of the most intense MS peaks. In this manner, the products are assigned according to Table 2-3. By far the most
abundant product is 1,3-butadiene, the most stable hydrocarbon with composition C₄H₆. This is the expected composition of the organic fragment arising from the dehydrohalogenation of I.

2.3.2 1,1-difluoro-2-chloroethene (II)

Photolyses of II were performed with the same technique used for I. Various pressures of II with a variety of buffer gases were photolyzed by focusing the approximately 0.4 J laser pulse with the 11.1" (28 cm) Ge lens. A summary of experiments on II is tabulated in Table 2-4.

One interesting feature of this system is the blue fluorescence observed around the focus of the beam. We have observed this effect in other vinyl halide systems; it has also been reported [2.3] in the MIRPA of chromyl chloride. In the latter system, the observed luminescence was attributed to excitation of a low-lying excited singlet state followed by fluorescence back to the ground state. In the olefin systems studied here, the lowest excited singlet states lie in the UV. The observed luminescence may come from highly excited fragments, but this conjecture has not been tested.

From the GCMS of several reaction mixtures, the products of the photolysis of II were identified. When II was photolyzed at 4.0 Torr with no added gas, the principal products were C₂F₄ (67%) and C₂F₃H (33%). A small amount of C₂F₂H₂ was also detected, but no C₂F₂ was found. When 14 Torr
Table 2-4. Summary of LID experiments on difluorovinyl chloride. All experiments were performed with the R(18) 10.6 laser line, 28 cm f.1. lens.

<table>
<thead>
<tr>
<th>Date</th>
<th>notebook</th>
<th>p(II) Torr</th>
<th>p(buffer)</th>
<th># shots</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/22/78</td>
<td>13W</td>
<td>10</td>
<td>0</td>
<td>1000</td>
<td>bright flashes; soot; HCl formed, other products</td>
</tr>
<tr>
<td>11/24</td>
<td>&quot;</td>
<td>1.8</td>
<td>0</td>
<td>1000</td>
<td>IR show products; no flashes</td>
</tr>
<tr>
<td>11/27</td>
<td>13Y</td>
<td>1.95</td>
<td>16.1 H₂S</td>
<td>1000</td>
<td>no flashes; GC taken, ambiguous results</td>
</tr>
<tr>
<td>12/4</td>
<td>14Y</td>
<td>2.15</td>
<td>9.0 &quot;</td>
<td>1500</td>
<td>very slight powder</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>2.25</td>
<td>6.2 NH₃</td>
<td>500</td>
<td>slight luminescence; white soot</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>2.2</td>
<td>4.1 MeOH</td>
<td>1500</td>
<td>blue fluorescence; problems with GC</td>
</tr>
<tr>
<td></td>
<td>15W</td>
<td>5.1</td>
<td>15.1 H₂S</td>
<td>&quot;</td>
<td>very slight powder; large energy deposition</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>5.05</td>
<td>14.3 MeOH</td>
<td>2000</td>
<td>tremendous attenuation of beam; fluorescence; GC shows massive peak in Rxn mixture</td>
</tr>
<tr>
<td>12/6</td>
<td>15Y</td>
<td>5.1</td>
<td>0</td>
<td>1000</td>
<td>same massive peak here too</td>
</tr>
<tr>
<td>12/20</td>
<td>16Y</td>
<td>4.15</td>
<td>13.1 H₂S</td>
<td>1500</td>
<td>white powder; GCMS done</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>4.0</td>
<td>0</td>
<td>1000</td>
<td>intense fluorescence; visible brown powder; GCMS</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>4.0</td>
<td>14.0 MeOH</td>
<td>1500</td>
<td>very slight powder; GCMS done</td>
</tr>
<tr>
<td>3/8/79</td>
<td>25W</td>
<td>4.25</td>
<td>14.35 D₂S</td>
<td>1500</td>
<td>thin blue fluorescence; audible signal; GCMS done</td>
</tr>
</tbody>
</table>
of methanol was added, however, the products $C_2F_2H_2$, $C_2F_3H$ and $C_2F_4$ were observed in ratios of 1:0.15:0.07 respectively. A very similar product mixture was observed when 13 Torr of $H_2S$ was used as a buffer.

The abundance of $C_2F_2H_2$ suggests that $CF_2C:$ formed in the dehydrohalogenation of II leaches hydrogen from the buffer gas. As a test of this hypothesis, $D_2S$ was used as the buffer gas. Amongst the reaction products was seen undeniable evidence of $C_2F_2D_2$. The mass spectrum did not reveal which isomer of $C_2F_2D_2$ was detected, but it is believed to be $CF_2CD_2$ from the weight of previous evidence.

2.3.3 1,1,1-trifluoro-2-iodoethane (III)

A few experiments on III were performed at pressures of 4 to 6 Torr with 0.4 J pulses of the 9.6 micrometer $P(18)$ laser line. The experimental apparatus was the same as used above. In all experiments, copious amounts of iodine were formed, as evidenced by dark crystals which formed near the center of the cell, where the beam waist occurs. No products were observed when the beam was not focussed.

Unlike other systems we studied, the primary species formed, presumed to be $CF_3CH_2$, undergoes considerable bimolecular addition to other fragments. The GC spectrum showed two close peaks, which, from MS analysis were shown to be $CF_3CH_2CH_2CF_3$ and $CF_3CH_2CF_2CFH_2$ or $CF_3CH_2CFHCFCF_2H$ respectively. The unambiguous identity of the component or
mixture in the second GC peak could not be determined because the cracking patterns of the two candidates listed above are almost indistinguishable. A possible mechanism which accounts for the observed products includes hydrogen and fluorine migration following the initial loss of iodine:

\[
\begin{align*}
\text{CF}_3\text{CH}_2\text{I} & \xrightarrow{\text{hv}} \text{CF}_3\text{CH}_2 + \text{I} \\
\text{IV} + \text{IV} & \rightarrow \text{CF}_3(\text{CH}_2)_2\text{CF}_3 & \text{(first gc peak)} \\
\text{IV} & \rightarrow \text{CF}_2\text{CFH}_2 & \text{(V)} \\
\text{IV} + \text{V} & \rightarrow \text{CF}_3\text{CH}_2\text{CF}_2\text{CFH}_2 \\
\text{V} & \rightarrow \text{CF}_2\text{HCFH} & \text{(VI)} \\
\text{IV} + \text{VI} & \rightarrow \text{CF}_3\text{CH}_2\text{CFHCF}_2\text{H}
\end{align*}
\]

While it is possible to account for all the possible products in this way, further experiments would be necessary to verify the various steps of this mechanism.

Loss of HI following MIRPA would lead to the stable product CF₂CFH₃, which may undergo further LID during subsequent laser shots. No C₂ species other than the parent molecule were detected in these experiments, but an analysis with greater sensitivity may detect them.

2.3.4 chlorocyclobutane (VII)

Under essentially the same conditions as used for III, VII was photolyzed with the P(18) 9.6 μ laser line. IR and GC spectra revealed four products: ethylene, acetylene, vinyl
chloride and 1,3-butadiene. These products are in concert with the results of King et al. [2.4] who observed two reaction channels in Very Low Pressure Pyrolysis (ULPP) of VII. One channel produces vinyl chloride and ethylene, and the other HCl and butadiene. The acetylene produced here presumably arises from photolysis of the primary photoproducts. Joseph S. Francisco is currently investigating this system in detail [2-5].
3.1 Chemical mechanisms

In the previous chapter and in Appendix A, the mechanisms by which vinyl chloride reacts were elucidated in fine detail. The principal mode of dissociation was found to be three centered molecular elimination of HCl. The data for cis-d_1-vinyl chloride are unambiguous on this point. The results of trans-d_1-vinyl chloride photolyses are discussed in detail in Appendix A.

In all of the systems studied, by far the greatest amount of reaction was seen to occur through the reaction channel having the lowest activation energy $E_a$. For the vinyl chloride system, isomerization was seen to be many times faster than the elimination channels at all $\langle E \rangle$. Molecular elimination of HCl was preferred over the higher energy Cl bond scission channel in the photolysis of CF_2CHCl.

Elimination of iodine from CF_3CH_2I occurs with such great efficiency that products which would result from the higher energy molecular elimination of HI were not seen at all. All evidence points to the conclusion that a reaction mechanism having lower activation energy barrier is favored over a mechanism having a higher energy barrier.

This, of course, is in concert with unimolecular reaction rate theory. As is evident from Fig. 3a in Appendix A, the
microscopic unimolecular reaction rates are very sensitive to their $E_a$, and only at extremely high internal energies $E_v$ do the rates converge. To accept that this behavior will be followed is tantamount to admitting that for this type of laser induced chemistry, mode specific reactions may never be possible. By this method of excitation, a low activation energy reaction channel cannot be bypassed in favor of another at higher activation energy merely because the initial vibrational excitation began in a particular set of vibrational modes. This point will be discussed further in the next section.

Evidence for the formation of the long-lived intermediate $F_2C=C$: is clear-cut, and is reviewed in Appendix B. As was shown there, evidence for the existence of its dimethyl counterpart $(CH_3)_2C=C$: is not as convincing. Use of the cyclopropenyl intermediate seems to be necessary, especially since it leads to many of the observed products:

\[
\begin{align*}
\text{(3-1a)} & \quad \text{---} \\
\text{(3-1b)} & \quad \text{CH}_3\text{CCH=CH}_2 \rightarrow \text{H}_2\text{C=CHCH=CH}_2 \\
\text{(3-1c)} & \quad \text{---}
\end{align*}
\]

In (3-1c), H migration across the double bond is required, and can be expected to occur readily, as seen in the photolysis of vinyl chloride to make acetylene.
It must also be stressed here that all of the laser-induced reactions reported in this thesis have been induced by other methods as well. Acetylene is formed in shock tube dissociation [3.1] of vinyl chloride; vinylidene carbene chemistry is well known in the liquid phase [3.2] and so on. No entirely new and exotic reactions have been performed using MIRPA. The reaction product mixtures may be different from those induced by other methods (such as by direct heating); this point will also be discussed in the next section.

3.2 Kinetic effects

3.2.1 Effects of the internal energy distribution

As Craig Jensen made clear in his thesis [3.3], first moments of a distribution do not uniquely determine that distribution. Specifically, the chemistry induced by a distribution of molecules over energy $P(E)$ produced in a MIRPA experiment is, in itself, insufficient to specify $P(E)$ uniquely. If the microscopic rates $k_{1}^{RRKM}(E)$ are well characterized for a system having $i$ channels of reaction, then a LID experiment may render as many as $i$ first moments:

$$k_{1}^{AVG} = \int_{E_{a1}}^{\infty} P(E) k_{1}^{RRKM}(E) dE \quad (3-2)$$

In the trans-$d_{1}$-vinyl chloride system, for example, three moments are determined, those being the average rates $k_{1}^{AVG}$ for isomerization, cis-elimination and gem-elimination.

However, much of the information gained by these $i$
moments of \( P(E) \) is redundant. Since only "hot" molecules react, the average rates \( k^{\text{AVG}}_1 \) determined by the net chemistry actually sample only the high energy portion of the distribution \( P(E) \). No information is gained for energies lower than the lowest \( E_a \), because the \( k^{\text{RRKM}}_1 (E) \) do not sample this portion of the distribution. When the \( E_a \) for simultaneous reactions are nearly equal, the \( k^{\text{RRKM}}_1 (E) \) sample a nearly identical portion of \( P(E) \); in this case, knowing two \( k^{\text{AVG}}_1 \) gains little more information than knowing only one \( k^{\text{AVG}}_1 \).

This is precisely the point of Fig. 4 of Appendix A. By using the chemical evidence alone we are not able to choose a particular form of the distribution. Both the Poisson and the maximum entropy distributions are capable of fitting the data. What is needed is an independent measurement of \( P(E) \), such as \( \langle E \rangle \) (the average energy of the distribution), which is sensitive to the entire distribution, not merely its high energy shape. If \( \langle E \rangle \) were known for the various conditions used in the photolysis of trans-\( \mathrm{d}_1 \)-vinyl chloride, this additional constraint would allow us to construct a distribution subject only to maximum entropy and the observed first moments \( \langle E \rangle \) and \( k^{\text{AVG}}_1 \). In effect the energy centroid of the distribution would be dictated by \( \langle E \rangle \) while the dispersion would be determined by the extent to which the distribution overlaps the \( k^{\text{RRKM}}_1 (E) \).

Experimentally, the value of \( \langle E \rangle \) may be very difficult to
measure. One technique [3.4] involves addition of a nonabsorbing "chemical thermometer" gas to the reaction cell. Since a very small fraction of the total distribution $P(E)$ reacts, most of the energy contained in the pumped molecules under study thermalizes via collisional $V\rightarrow V,R,T$ relaxation. A small amount of gas not affected by the particular laser frequency would come to the same vibrational temperature as the directly pumped molecules, and hopefully would react before $V\rightarrow T$ deactivation occurs. The extent of reaction of the "thermometer" molecules is then compared to a thermal average rate, thus determining $\langle E\rangle$ for the total sample.

Since this method is inherently collisional, and occurs over the entire volume of the cell, it renders a value of $\langle E\rangle$ equivalent to the gross amount of energy absorbed averaged over the entire sample. In a given system, however, only a small portion of molecules in the cell are irradiated by the laser beam, and only a fraction of these molecules undergo MIRPA [3.5]. It is the $\langle E\rangle$ of this fraction which we would like to measure, since these are the molecules in the distribution prepared by the laser pulse. This method, if not corrected for these effects, can be expected to give consistently low values of $\langle E\rangle$.

There is another method of determining $\langle E\rangle$ which at least in principle can determine $\langle E\rangle$ for an arbitrarily small volume of sample in the laser beam. This method is Gaussian deconvolution; it is discussed mathematically in Appendix D
and is applied to this particular problem in the following chapter. It should be noted that this method was not developed until roughly two years after the vinyl chloride work was completed.

3.2.2 Rates of laser pumping and intramolecular vibrational relaxation

To model a LID kinetic system completely, one must incorporate the full time evolution of the system rather than "freeze" it into a quasi-static state, as we have done with the vinyl chloride model. The time dependence of the MIRPA process during the laser pulse, energy flow into nonresonant vibrational modes, collisional activation/deactivation and other processes must be included in the total picture. Since so many distinct processes are involved in a typical MIRPA event, a model incorporating a great number of kinetic processes explicitly would easily require more rate constants than are available or even determinable for a given system. This extreme complexity may be worth less than a much simpler approach, such as the one we have used for vinyl chloride.

Several authors have investigated various methods of modelling the time dependence of the MIRPA-LID process. Lyman [3.6] and others [3.7] have approximated their systems with a Master Equation formalism. A harmonic energy grid is constructed which is resonant with the laser field. The rates of pumping population between successive levels are determined
by approximating the dipole matrix element in an astute fashion, by including collisional coupling between levels by V-V energy exchange, and by careful inclusion of the proper degeneracies of each level. Although these models can be adjusted to reproduce a variety of data, such as energy deposition as a function of pressure or laser intensity [3.6], the distribution predicted by the Master Equation approach never deviates appreciably from a Poisson. This may be a consequence of the harmonic grid necessitated by this method; coherently pumped harmonic oscillators produce a Poisson distribution analytically [3.8]. This model also neglects all rotational relaxation effects.

More complex models, which have included rotational hole burning and relaxation, have been demonstrated by Cantrell and coworkers [3.9] for SF₆. These models utilize the elegant angular momentum algebra of octahedrally symmetric molecules, and have addressed the frequency and intensity dependence of energy deposition and dissociation efficiency. Many other investigators have proposed models specific to SF₆; Jensen gives a sweeping review of these in his dissertation [3.3].

What would be of greater value to our understanding of LID as a general process is a model general enough to be applicable to any molecule yet simple enough to be useful with a minimum of spectroscopic and kinetic data. Ackerhalt and Galbraith [3.10] have introduced a model which, they claim, meets these expectations. It includes both coherent and
incoherent laser pumping, intramolecular vibrational relaxation into many separate vibrational ladders, unimolecular reaction kinetics and a minimum of empirically determinable parameters. It has been successfully applied to SF$_6$ (of course!) and the authors claim that it is flexible enough to accommodate many different types of molecules.

The situation remains, however, that for most molecules whose LID has been studied, even the few parameters needed for a model such as that of Ackerhalt and Galbraith are not known. Moreover, determining these parameters and calculating predictions with abandon may not be lucrative or meaningful. In many cases, a "rule of thumb" would suffice to understand and predict the qualitative response of a chemical system; a flowchart of this nature has been provided recently by Thiele, Goodman and Stone [3.11] and is depicted in Fig. 3-1.

The reasoning behind Fig. 3-1 is straightforward. If intramolecular vibrational relaxation (IVR) is faster than the laser pump rate (LPR), energy deposited in the molecule randomizes amongst all vibrational modes as quickly as it is absorbed. No mode selective chemistry can be expected. Similarly, if IVR is faster than the dissociation rate (DR), vibrational energy will be randomized before reaction will occur, and no selective chemistry will occur. If, however, IVR is slower than both LPR and DR, vibrational energy will not be able to leak out of the set of modes directly pumped by the laser before dissociation occurs. In this case,
selectivity is possible (but not guaranteed) because only a few modes contain relatively large amounts of excitation. If DR is faster than LPR, however, molecules will react as soon as they absorb sufficient energy to surmount the lowest E barrier. In this case the products will be very similar to those produced in thermal reactions. If LPR is faster than DR, molecules may absorb much more energy than the lowest E barriers, and higher energy channels normally never sampled by thermal reactions become available. A semi-selective, definitely nonthermal mixture of products would be seen in this case.

All of the laser induced chemistry reported here is consistent with this reasoning. The vinyl chloride work would seem to fall in the upper left hand box of Fig. 3-1, "NO SELECTIVITY." Other systems, such as the cyclobutyl chloride system mentioned in Chapter 2, have demonstrated a nonthermal distribution of products and thus fall in the lower right hand box. These systems are currently under continued study.

3.3 Energy disposal in fragments

Another consequence of falling into the lower right hand box in Fig. 3-1 is that when the molecule dissociates, an excess energy \( \Delta E \) given by

\[
\Delta E = E_v - \Delta H \tag{3-3}
\]

is partitioned amongst the degrees of freedom of the
Fig. 3-1. Flowchart for determining the roles played by various kinetic processes in determining the products seen in an LID experiment.
fragments. In Eqn. 3-3, $E_v$ is the vibrational excitation forced into the molecule before it undergoes a reaction having net enthalpy $\Delta H$. Fragments can be expected to be born vibrationally "hot" even for endothermic reactions; additional absorption of photons by these "hot" fragments and secondary reactions may also occur.

The precise partitioning of excess energy amongst the dissociation products has been studied for a few systems, such as for $\text{CF}_2\text{HCl}$ [3.12]. This molecule dissociates into $\text{CF}_2$ and $\text{HCl}$; the internal energy content of the former species was measured spectroscopically by laser induced fluorescence. It was found that a considerable amount of energy was partitioned into translation (approximately 7 Kcal/mole) and that the distributions of vibrational and rotational energy could be described by a probability $p(E)$ of the form

$$p(E) \propto \exp(-E_b/kT_b)$$

(3-4)

where $b$ is $V$ for vibration or $R$ for rotation. Typical average energies for this system are listed in Table 3-1. Similar behavior was observed for the LID of $\text{CF}_2\text{Br}_2$ and $\text{CF}_2\text{Cl}_2$ [3.12].

The energy partitioning into the $\text{CF}_2$ radicals described above suggests that partitioning of energy into the various degrees of freedom of the fragments of LID is statistical, that is, constrained only by the total energy available. If this is the case, one would expect that fragments of comparable vibrational and rotational complexity would be
Table 2-1. Distribution of energy in the nascent CF₂ fragment formed in the LID of CF₂HCl, CF₂Br₂ and CF₂Cl₂. Data are taken from J. C. Stephenson and D. S. King, J. Chem. Phys. 69, 1485 (1978) © 1978 American Institute of Physics

<table>
<thead>
<tr>
<th></th>
<th>CF₂HCl</th>
<th>CF₂Br₂</th>
<th>CF₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>TV (K)</td>
<td>1160</td>
<td>790</td>
<td>1050</td>
</tr>
<tr>
<td>EV (kcal/mole)</td>
<td>3.6</td>
<td>1.8</td>
<td>2.9</td>
</tr>
<tr>
<td>TR (K)</td>
<td>2000</td>
<td>450</td>
<td>550</td>
</tr>
<tr>
<td>ER (kcal/mole)</td>
<td>6.0</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>TT (K)</td>
<td>2300</td>
<td>570</td>
<td>510</td>
</tr>
<tr>
<td>ET (kcal/mole)</td>
<td>6.9</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>E avg (kcal/mole)</td>
<td>16.5</td>
<td>4.9</td>
<td>6.0</td>
</tr>
</tbody>
</table>
awarded equivalent amounts of energy. A comparison of the average amounts of energy partitioned into the CF<sub>2</sub> fragments from CF<sub>2</sub>Br<sub>2</sub> and CF<sub>2</sub>Cl<sub>2</sub> shown in Table 3-1 is in concert with this assumption.

In Appendix B we comment on the effect of excess energy partitioning on the ability of fragments R<sub>2</sub>C=C: to rearrange. In the case of the hypothetical H<sub>2</sub>C=C:, the barrier to rearrangement is only a few Kcal/mole [3.13]. The fragment is expected to contain a comparable amount of vibrational energy, and hence the rearrangement should occur easily. If the conjecture that energy partitioned into the vibrational degrees of freedom is proportional to the number of vibrational states available, then we would expect that the F<sub>2</sub>C=C: species would be born with a vibrational energy comparable to the H<sub>2</sub>C=C: species. Since the barrier to rearrangement for F<sub>2</sub>C=C: has been calculated [3.14] to be much greater than the few Kcal/mole needed for H<sub>2</sub>C=C:, we concluded that the former species was born with a small amount of internal energy, insufficient to surmount the barrier for rearrangement.

The greater vibrational complexity of (CH<sub>3</sub>)<sub>2</sub>C=C:, compared to H<sub>2</sub>C=C: and F<sub>2</sub>C=C: should lead to a partitioning of a much greater fraction of the excess energy into the first-named species. This is graphically illustrated in Fig. 3-2, where the number of vibrational states available per Kcal/mole is plotted as a function of internal energy E<sub>v</sub>. We
conclude from Fig. 3-2 that the enormous amount of "vibrational heat capacity" of \((\text{CH}_3)_2\text{C}=\text{C:}\) will sink much more excess energy than the other two vinylidene carbenes. What we observe chemically is that the dimethyl species sinks enough energy to surmount the barrier to rearrangement, which we estimate in Appendix B to be 10-15 Kcal/mole. From this we conclude that, in the absence of quantitative data to the contrary, energy partitioning amongst these LID products is consistent with simple statistical behavior.
Fig. 3-2. Density of vibrational states per Kcal/mole as a function of the internal energy $E_v$. The expression for $\gamma_v$ used to calculate these curves is the same as that used in Appendix A:

$$
\gamma_v = \frac{(E_v + aE_z)^{s-1}}{(s-1)! \sqrt{2 \pi h \nu_v}} \left[ 1 - \beta \frac{dW}{dE_v} \right]
$$

This is the Whitten-Rabinovitch density of states function*; the definitions of parameters $E_z$, $E'$, $a$, $\beta$ and $W$ can be found in Appendix A; $s$ is the number of vibrational modes having frequencies $\nu_v$. The vibrational frequencies used in these calculations are contained in Table 3-2.

Table 3-2. Vibrational frequencies used in the calculation of Fig. 3-2.

<table>
<thead>
<tr>
<th>H₂C=CH₂</th>
<th>F₂C=CF₂</th>
<th>(CH₃)₂C=C=CH₂</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>3089</td>
<td>1795</td>
<td>1650</td>
<td>vibrational</td>
</tr>
<tr>
<td>3037</td>
<td>1680</td>
<td>420</td>
<td>frequencies</td>
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<td></td>
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<td>1100</td>
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</tr>
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<td>1036</td>
<td>1205</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>897</td>
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<td></td>
<td>200</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>1450</td>
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<td></td>
<td></td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>1195</td>
<td></td>
<td>1195</td>
<td>doubly</td>
</tr>
<tr>
<td>1475</td>
<td></td>
<td>1475</td>
<td>degenerate</td>
</tr>
<tr>
<td>1471</td>
<td></td>
<td>1471</td>
<td>vibrations</td>
</tr>
<tr>
<td>1430</td>
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</tr>
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<td>2964</td>
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<tr>
<td>2982</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1.0372</td>
<td>0.8753</td>
<td>1.2844</td>
<td>β</td>
</tr>
<tr>
<td>15.66</td>
<td>12.04</td>
<td>48.25</td>
<td>Eₗ, Kcal/mole</td>
</tr>
<tr>
<td>1.80E19</td>
<td>6.43E18</td>
<td>1.60E73</td>
<td>τᵣ, (cm⁻¹)s</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>24</td>
<td>s</td>
</tr>
</tbody>
</table>

These frequencies were obtained by reading absorption spectra of the parent molecule from standard IR spectra taken at MIT. Frequencies assigned to bands arising from =CCl-H and =C-Cl stretches and bends were then cast out.
Chapter 4. Gaussian Beam Deconvolution

4.1 Basic method

In the previous chapter we concluded that chemical evidence alone is insufficient to determine uniquely the distribution $P(E)$ of molecules over energy produced in a MIRPA event. Additional experimental evidence, such as a determination of $\langle E \rangle$, is required before quantitative statements can be made about the shape of $P(E)$. In particular, a determination of $\langle E \rangle$ accurate to within a factor of two would be necessary to choose between Poisson and maximum entropy distributions for the trans-$d_1$-vinyl chloride system.

The difficulty of measuring $\langle E \rangle$ directly can be appreciated when one realizes where in the laser beam molecules that undergo transformation are located. In a weakly focused beam, intensities sufficiently high to cause MIRPA and consequent reaction are located at or near the focal point. The actual volume inside the beam which contains the reacting species may be very small [4.1] (typically $0.01 \text{ cm}^3$) compared to the total volume swept out by the beam inside the reaction cell ($\sim 100 \text{ cm}^3$). A measurement of the total energy deposited in the entire sample would not render a value of $\langle E \rangle$ for that small volume of reacting species because much of the energy is deposited in molecules in the lower intensity
portions of the beam and does not lead to LID.

What we seek is a method of determining the response of the system at particular fluences although our measuring technique renders the response over the entire fluence range intercepted by the sample. Since the intensity profile of a "TEM$_{00}$" Gaussian laser beam is known analytically for all points in the beam [4.2], it might be possible to deconvolute the data to reveal system response at discrete fluences (or intensities). The technique, in fact, has been elucidated by Kolodner et al. [4.3] and by Reiser and Steinfeld (Appendix D) and has been used by Herman [4.4]. The reader is invited to read Appendix D to familiarize himself with Gaussian beam optics and to glean the salient mathematical details of the technique.

Basically, the deconvolution procedure relies on the fortuitously simple form of a Gaussian beam profile to unfold the response of the system analytically. Any given measurement using a Gaussian beam, for example, a measurement of total absorption, contains two kinds of information: that which determines the absorption at discrete fluences $<n>(\phi)$ and the geometry of the fluence profile in the beam $\phi(x,y,z)$. By doing a series of experiments in which an appropriate parameter, such as the net energy per laser pulse, is systematically varied, the clever experimenter can effectively subtract the profile information $\phi(x,y,z)$ by taking the difference between adjacent points. The fortuitous nature of
the mathematical formalism allows us to use the local slope
\( \frac{\partial (\text{energy deposited})}{\partial (\text{total pulse energy})} \) and experimentally
determinable constants to effect the "subtraction" of the
Gaussian fluence profile. The simplicity of the procedure can
be seen in the section entitled "Treatment of Experimental
Data" in Appendix D.

Nearly any experimental effect which is fluence or
intensity dependent can be studied with this technique,
provided that the total response is detected over the entire
portion of the laser beam intercepted by the sample. For
determining \( \langle n \rangle (\phi) \), transmission measurements may be
difficult when the beam intensity is very large and energy
deposition is small. Optoacoustic detection is a more
appropriate method of measurement in this case, and has been
used with Gaussian beam deconvolution of experimental data by
Black et. al. [4,5].

Other effects can also be studied. The intensity
dependence of multiple (visible) photon ionization could be
determined by placing electrodes around the laser beam to
measure net ionization current. Laser induced fluorescence or
laser induced collisions could be studied provided that
integrating optics are used to collect fluorescence from all
portions of the beam. Nonlinear optical phenomena, such as
frequency multiplying or mixing, could be studied in fine
detail without the need to describe the input beam intensities
by cross sectional averages.
4.2 Experimental difficulties

Since the deconvolution technique inherently relies on taking the slope of an experimentally determined curve, the precision of the deconvoluted data is severely affected by the precision of the original data. Small differences between large numbers can be quite noisy, and for this reason Black [4.5] fit his experimentally determined curve with a convenient algebraic function before taking the slope analytically. Generally a trick of this sort is always possible by fitting the observed data to an n-degree polynomial [4.6] which is guaranteed to have an easily determinable, continuous first derivative.

When the observed data are sparse, however, experimental precision ultimately limits the value of the deconvoluted data. As an example let us consider the energy deposition example used in Appendix D, i.e. multiple photon absorption in SF, when small uncertainties are imposed upon the "observed" data. In this case, a precision of a few percent in the measurement of the total energy deposited in the SF sample implies that deviations of a few percent from the observed value are statistically not meaningful. If a demon were to remove absorbing molecules from the focal point of the beam, where we are most interested in the absorption function \( \langle n \rangle (\phi) \), such that the net energy deposited changed by only a few percent, our measurement would not be statistically different. In a qualitative way, then, we see that the
precision of the experimental determination limits the precision with which we determine \(<n>(\phi)\), which we translate into a geometrical volume. Uncertainty in the observed information implies uncertainty in the deconvoluted information.

We can use the numerical example of Appendix D to illustrate these statements graphically. Let us suppose that we performed an experiment using a 28 cm focal length lens to focus a pulsed CO\(_2\) laser beam into a sample of SF\(_6\), whose absorption is given by \([4.5]\)

\[
<\alpha>(\phi) = 9.15\phi, \quad 0 \leq \phi \leq 2.55
\]

\[
= 14.1(\phi + 0.084)^{1/2}, \quad \phi \leq 2.55
\]

\[
+ 0.51 \quad \text{J/cm}^2
\]

Using a simple convolution equation,

\[
E_D \leq \int_{\phi_m}^{\phi_0} <\alpha>(\phi) v(\phi) \, d\phi
\]

(4-2)

where \(\phi_m\) is a convenient lower bound of the fluence (taken to be 0.01 J/cm\(^2\)), \(\phi_0\) is the peak fluence (9.42 J/cm\(^2\) for a pulse energy of 10 mJ) and \(v(\phi)\) is given by Eqn. (24) of Appendix D appropriate for a 28 cm focal length lens, we can numerically compute the total energy deposited in the sample \(E_D\). We then change the upper bound of Eqn. (4-2) so that the calculated energy deposited \(E_D'\) is, for example, 95% of \(E_D\). This means that we have calculated the energy deposited throughout the beam except in the last small volume near the focal point. This volume \(V(\phi')\) is easily calculated by Eqn. (16) of Appendix D) the energy deposited in this
volume \( V(\phi') \) is equal to the precision of the determination of \( E_D \). \( V(\phi') \) is plotted against the precision in Fig. 4-1.

As we see in Fig. 4-1, if our "measurement" of \( E_D \) were infinitely precise, we could determine the \( \langle n \rangle(\phi) \) for a vanishingly small volume of sample. As the precision degrades, however, the corresponding uncertainty in the geometrical information increases, so that the deconvoluted data will give the response \( \langle n \rangle(\phi) \) averaged over the interval \( \phi' \leq \phi \). Eventually this imprecision becomes unacceptable, for instance, when \( \phi' \) reaches the threshold fluence for dissociation, which is approximately 1 J/cm\(^2\) for SF [4.7]. This point is marked with an arrow in Fig. 4-1. We conclude that only for highly precise measurements of \( E_D \) can the deconvolution technique be of value.

As is clearly stated in the "Treatment of Experimental Data" section of Appendix D, Gaussian beam deconvolution renders the average response \( \langle n \rangle(\phi) \) over whatever distribution of molecules over absorbed energy \( P(E;\phi) \) is formed when an ensemble of molecules is subjected to a uniform fluence \( \phi \). This technique can never give information about the shape of \( P(E;\phi) \). The information obtained, such as \( \langle n \rangle(\phi) \), must be combined with other data, such as data from LID experiments discussed in the previous two chapters, to obtain a clear understanding of the distribution \( P(E) \).

Ideally one would like to measure \( P(E) \) directly, and for this we must turn to more elegant spectroscopic techniques, which
Fig. 4-1. Minimum volumes $V(\phi')$ discernable by deconvolution of a Gaussian beam for experiments of finite precision. Details of the calculation are given in the text.

we begin to discuss in the following chapter.
5.1 Introduction

Thus far in this thesis we have investigated MIRPA by studying net chemistry or net absorption in typical systems. The information obtained is necessarily an average over the range of fluence, intensity and time dependent processes which contribute to the net LID results. As we concluded in Chapter 3, chemical evidence alone is insufficient to elucidate the fine details of the dynamics of MIRPA events, even when aided by techniques such as Gaussian beam deconvolution.

Ideally we would like to understand the nature of the MIRPA phenomenon on a fundamental level. Specifically, we would like to answer such questions as by what route do the molecules absorb the first few photons, what roles are played by vibrational anharmonicity and by rotational compensation, how fast does rotational hole filling occur, at what energies does intramolecular vibrational relaxation become fast, and is there a good method of predicting pressure effects. Ultimately our goal would be the ability to predict the types of chemistry we expect from a particular system from fundamental spectroscopic evidence, given a reasonably general framework such as Fig. 3-1.

To answer the questions raised above one must directly interrogate molecules which are being subjected to the very
intense infrared laser fields used in MIRPA and LID experiments. This implies the use of a spectroscopic probe to monitor the molecular behavior during excitation by an intense pump field. Since in many systems used in LID experiments no easily accessible electronic states exist, visible probe radiation is of only limited usefulness. The technique of choice is infrared-infrared double resonance, wherein the infrared spectroscopic probe monitors vibrational populations affected by the application of the infrared pump field.

This technique was first used by Steinfeld and coworkers (5.1), who used two CO\textsubscript{2} lasers as pump and probe beams in SF\textsubscript{6}. This work and that of others (5.2) was restricted to probing at the small number of discrete frequencies to which CO\textsubscript{2} lasers can be tuned. The use of a tunable narrow linewidth diode laser has vastly increased the spectroscopic information gained by the double resonance technique, as has been demonstrated by Moulton and Mooradian (5.3). Our own work on diode-infrared laser double resonance (DILDOR) in SF\textsubscript{6}, begun by Jensen (5.4), has been reported and is included in this thesis as Appendix E, which the reader is urged to peruse.

The present DILDOR experiments are designed to probe the absorption dynamics of the first one or two photons. The interaction of the pump field with individual absorption features can be easily monitored, and a wealth of dynamical information has been recovered. The salient features of the experimental apparatus, procedure, results and discussion are
contained in Appendix E. To avoid repetition, experimental details not mentioned in Appendix E, results on DILDOR in ammonia, and further discussion of a few details of data interpretation will form the bulk of this chapter.

5.2 Experimental details

Working with a diode laser can be a very tedious and aggravating experience. As is mentioned in Appendix E, diodes must be kept cold to insure their survival, although they must be warmed to room temperature periodically. As air leaks into the cold head vacuum jacket, a gradual temperature rise can be noticed over a period of weeks. When the temperature reaches 15-20 °K, the cold head must be warmed (to insure that moisture will be removed), evacuated and rechilled. Care must be taken to avoid backstreaming pump oil into the cold head.

Occasionally the cold head will "ratchet" upon startup, producing a grunting noise. This is an indication that a foreign substance, such as dust or moisture, has found its way into the helium flow and is lodged in the cold head. Replacing the helium in the cold head after disconnecting it from the refrigerator is the only known cure, short of having the cold head rebuilt.

To date no means of detecting the diode beam other than with a cryogenically cooled semiconductor detector has been found. If the diode beam is found, it must be traced around the table using apertures to reveal the beam position. A HeNe
laser beam can be superimposed on the diode beam to act as a tracer, but usually the diode beam must be traced with an iris after the first two mirror reflections. The HeNe beam can then be used to trace a path to the remaining mirrors, through the monochromator and onto the detector.

Once the diode beam is routed through the monochromator, a series of scans must be made to determine the frequencies over which the diode lases. This is a rather tedious operation; it involves systematically changing the diode temperature, while making a current scan with the monochromator slits wide (about 2 mm), moving to a different monochromator setting, scanning again, etc., for each temperature. A range of currents and temperatures can then be selected to determine if the laser has a mode at the precise frequency desired.

An important diagnostic at this point cannot be overlooked. It is mandatory that an etalon scan must be made when a mode is located at the correct frequency. Many times the mode is not "pure", that is, it contains two modes at nearly the same frequency which tune in unison. Often a mode may "hop", or jump to another frequency, so that a continuous current scan is not continuous in frequency. The etalon fringes are currently the only method we have to interpolate between reference frequency absorption lines.

A disturbing feature in the present system is the current ripple in the scanning current power supply, an Arthur D.
Little TDLS-II. This ripple was measured to be approximately 0.15 mA peak to peak. A typical diode mode tuning rate of 0.12 etalon fringes/mA (one fringe equals 0.65 cm^-1), the measured ripple implies a peak to peak frequency jitter in the diode mode of 26 MHz. This will be an important consideration in the following chapter.

Care must be taken to avoid grounding either of the recorder output jacks on the TDLS-II. For this reason, the variable dc offset voltage supply has been floated from ground. This supply is placed in series with the recorder output voltage. In this way, tuning ranges of a few hundred mA can be recorded using the entire useful X-scale range of the X-Y recorder. The variable dc voltage supply effectively extends the range of the "zero" knob on the recorder.

Several features of the Q-switched CO₂ laser must be noted. The optimum mixture of gases is approximately 4:1:1 for He, CO₂ and N₂ respectively, at a total pressure of 8 Torr. Dirt which collects on the ZnSe windows is most easily removed by applying water and Pex detergent with cotton. Effective c.w. power at a repetition rate of 125 Hz is typically 300 mW for the 10.6 micron P(18) line. We have measured a c.w. output on this line in excess of 30 Watts.

The diameter of the Q-switched beam is easily measured with a variable aperture. A power meter is placed behind an iris diaphragm mounted on an X-Y translation stage. The iris is placed over the center of the beam. The power transmitted
through the iris is then measured by the power meter as a function of the iris diameter. This function can be compared to the known [5.5] transmittance of a Gaussian beam of spotsize $\omega$ through an aperture of diameter $d$,

$$\text{fraction transmitted} = 1 - \exp(-d^2/2\omega^2) \quad (5-1)$$

In this manner, the spotsize of the Q-switched beam was found to be 2.5 mm for the work reported in Appendix E.

It is possible to align the pump and probe beams so well that they cannot be separated at the cold head (see Fig. 1 of Appendix E). A $1^\circ$ misalignment is sufficient to effect the required separation. A gold coated mirror is necessary to eject the Q-switched beam from the apparatus; mirrors of lower quality cause unwanted scattering. Stray reflections of the pump beam have caused serious frequency and intensity fluctuations in the diode beam; the amount of care required to minimize stray reflections cannot be overstressed. For example, the pump beam must strike mirrors in the center (which necessitates, in some cases, placing the probe beam near the mirror edges) to avoid reflections from the mirror edges and mounts.

Synchronization of the boxcar integrator with the laser pulse is accomplished with the circuit shown in Fig. 5-1. Trigger jitter is minimized when the negative-going trigger pulse occurs 15-30 $\mu$sec before the laser pulse. Generally it is impossible to keep this interval constant before 7 PM on
Fig. 5-1. Circuit diagram and optical configuration for Trigger pulses from the Q-switched CO$_2$ and N$_2$O lasers. Q1, Q2 - phototransistors; B1, B2 - 6V light bulbs; M1 - concave mirror; M2, M3 - rotating mirrors; L1, L2 - lenses.
weekdays. Apparently the speed of the mirror motor changes slightly with changes in wall socket voltage even though a massive voltage regulator is used to power the motor. Tweaking the grating alignment and minimizing the delay between trigger and laser pulses may help.

Brewster windows and grating lines insure that the pump field is horizontally polarized. Although polarization may not be the same for all diode lasers, diode beams are usually well polarized in the plane of the junction [5.6], or vertically polarized in the lab frame. This is not mentioned in Appendix E, and may have considerable impact on DILDOR signals. It will be discussed further in the following chapter.

5.3 Additional discussion

All of the SF₆ DILDOR spectra worthy of note are contained in the various figures of Appendix E. All spectra were taken with the same diode laser (now dead) in the same mode. This mode, the SF₆ spectrum inside it, and the assignments of the lines (courtesy of Dr. R. S. McDowell of the Los Alamos Scientific Laboratory) are exhibited in Fig. 5-2.

With the aid of hindsight, after completing the calculations to be presented in the following chapter, a few of the finer points of discussion in Appendix E should be reviewed. One of these points pertains to the field-induced
Fig. 5-2. Absorption spectrum of 0.08 Torr SF$_6$ in a 30 cm long cell. Top trace shows diode laser mode tuning curve (no cell in beam path). Lower trace shows etalon scan for a 1" Ge etalon (f.s.r. = 0.0499 cm$^{-1}$). Assignments courtesy of R. S. McDowell of Los Alamos. Frequency markers in cm$^{-1}$ are shown at the bottom of the graph.
mixings which supposedly were responsible for the satellite structure around the main feature of the 2-level double resonance (2LDR) and 3-level double resonance (3LDR) spectra (see Figs. 2 and 7 respectively in Appendix E). As we will show in Chapter 6 and Appendix H, these mixings do not explain the satellite structure. The matrix elements which are responsible for the "weak transitions" in SF$_6$ [5.7] do not play the significant role originally believed in Appendix E. This will be placed on more quantitative footing in the following chapter.

Up to now, collisions were not thought to be important within the 0.5 µsec time scale of these experiments. This may not be entirely correct, given that the rotational relaxation time of the 3LDR signal, $t_{3\text{-level}}$, was measured to be 0.54 µsec. Since this represents the time required for a $1/e$ refilling of the population of a single rotational state, collisions effecting rotational relaxation are seen to operate on precisely the time scale of the experiment. Hence, a detectable amount of rotational relaxation should occur within the time of the boxcar gate.

This conjecture is born out by the 4-level double resonance (4LDR) recorded by Jensen, which appears in Fig. 9 of Appendix E. In these spectra, SF$_6$ was pumped in the P(33) and P(32) manifold while the probe interrogates the R(45)-R(52) manifolds. Extensive signal is seen even at "zero" delay with respect to the laser pulse; one microsecond
later, rotational relaxation has depleted the entire \( J=45 \) to \( J=52 \) region. Thus, collisions are seen to change \( J \) by 10 to 15 quanta at a very rapid rate. One must assume that relaxation within a single \( J \) manifold in the ground state, where all \( K \) are nearly degenerate, occurs on a similar time scale, if not faster.

One must be clever enough, however, to avoid the implication that relaxation out of or into levels directly pumped by the laser occurs exclusively to the nearly isoenergetic levels which are also probed. It seems more likely that relaxation occurs by exchange of energy with a rotational "heat bath" in a process like that depicted in Fig. 18 of Appendix E. This "heat bath" is composed of molecules not pumped by the laser, including the \( \sim 60\% \) of the total room temperature population lying in hot bands, and ground state molecules having \( J \) far from the \( J \)'s resonant with the pump laser. When a depleted ground state rotational level is filled, the population comes largely from the "heat bath" and not from nearby levels exclusively. Steinfeld and coworkers [5.1] used this model to explain their early work in \( SF_6 \).

A stringent test of the collisional nature of this relaxation process would be to repeat the experiments at lower temperatures, where collision rates are lower. A corresponding increase in \( T_3 \)-level should be observed, as well as an absolute decrease in 4LDR activity in \( J \) manifolds far from resonance. These experiments are currently under way.
5.4 DILDOR attempts in NH₃

Microwave-infrared laser double resonance (5.8) has been observed in NH₃ using the N₂O P(13) laser line at 927.739 cm⁻¹, which is nearly resonant with the ¹⁴NH₃ ν₂ [qQ_ (8,7)] transition and the N₂O P(15) line at 925.979 cm⁻¹, which is 332 MHz lower than the ¹⁵NH₃ ν₂ [qQ_ (4,4)] transition. This suggests that a 2-level DILDOR might be observable as well. This system has the advantage that the lineshape of a single absorption feature may be recovered without the forest of interfering structure seen in SF₆.

A Q-switched N₂O laser was resurrected with the help of Tom Anderson and pressed into service. Its configuration is nearly identical to that of the Q-switched CO₂ laser, excepting that a 4.25 m radius rotating mirror is used (instead of 10 m radius). Details of its operation have been placed in Appendix I. Since this laser operated at 58 Hz and has less gain than the CO₂ laser, the usual power meter could not be employed to measure the average pulse power. Using a Gen Tec joulemeter, the total pulse energy was estimated to be 0.1 mJ; a typical c.w. output is 2-3 W (as compared with 30 W for the CO₂ laser). From this we estimate that the average pulse intensity is about a factor of ten lower than its CO₂ counterpart.

The experimental schematic is shown in Fig. 5-3. Aside from using the N₂O laser as a pump source, all other features of the apparatus are essentially the same as for DILDOR in
Fig. 5-3. Schematic of the apparatus used for N₂O laser-diode laser double resonance in NH₃. SCPS - scanning current power supply; DL - diode laser; I - irises; L1 - 5 cm f.l. collimating lens; M - flat gold coated mirrors; M1 - spinning 4.25 m radius mirror; M3 - paraboloid collecting mirror; MONO - monochromator; D - HgCdTe detector; AM - amplifier; BC - boxcar integrator; Y - X denotes axes of the x-y recorder; GT - 1.5 m gain tube; GR - grating; LB - light bulb; PD - photodiode. Electrical signals: A - diode laser current supply; B - trigger pulse; C - detector output.
Addition of collimating lenses was necessitated by the greater divergence of the N$_2$O laser beam. Intensities in the sample cell reached $\sim 1$ kW/cm$^2$.

That the N$_2$O P(13) line is very nearly resonant with the NH$_3$ (8,7) feature is clearly evident in Fig 5-4; Shimizu and Oka [5.8] estimate that the line centers are 10 MHz apart. Records of DILDOR in 1 Torr of NH$_3$, however, were disappointingly blank and showed no apparent signal above the noise level, as can be seen in Fig. 5-5. Several attempts were made and all met with a similar degree of success.

One may wonder why DILDOR was not successful when the microwave experiment was. A few calculations and the hindsight gained from the lineshape analysis presented in Chapter 6 can show that the DILDOR signal may be smaller than the noise recorded in Fig. 5-5. Since the dipole moment for NH$_3$ is 0.2 Debye [5.8] and the pump laser power is one tenth of that used for the SF experiments, we can estimate that the Rabi frequency $\Omega$,

$$\Omega = \frac{\hat{m} \cdot \hat{E}}{2 \sqrt{3} \ h}$$

(5-2)

where $\hat{E}$ is the electric field vector, was at least a factor of six smaller than in the SF$_6$ experiments. From the lineshape modeling of the SF spectra (detailed in Chapter 6), $\Omega$ for the NH$_3$ experiment should be 10-15 MHz.

An estimate of the homogeneous linewidth can be had by considering the hard-sphere collision rate [5.9] for NH$_3$ at 1
Fig. 5-4. Absorption (downward deflection) of 40 Torr $N_2O$ in a hot cell in the region of the $P(13)$ laser line (lower trace). Also shown is the feature $^1_2 (8,7)$ in 1 Torr of $NH_3$ (upper trace). Diode current and frequency increase to the right.
Fig. 5-5. DILDOR attempts in NH$_3$ using an N$_2$O laser. Absorption trace (a) was taken in 1 Torr of NH$_3$ over the same transition as shown in Fig. 5-4. Two DILDOR scans were then made, traces (b) and (c). Finally, trace (d) was recorded (absorption again) to indicate the amount of drift in the diode laser tuning curve. In (a) and (d), absorption is a downward deflection; in (b) and (c), downward deflections would correspond to transient transparency, or saturated absorptions.
$\text{N}_2\text{O} \text{ miran inhal}$
\[ z = \frac{4d^2 \sqrt{kT}}{mN} \]  

which renders, for diameter \( d = 4 \) Ångstroms at room temperature,

\[ z \approx 15 \text{ MHz} \]

For comparison, the Doppler width of the transition is 40 MHz FWHM [5.8]. From these estimates, we conclude that the pump laser intensity in this case is sufficient to saturate only a single velocity group of the entire Doppler contour. This velocity component is 10 MHz from line center, where the Doppler profile is down to \( \sim 60\% \) of its peak value.

Furthermore, the effective linewidth of the probe laser will be estimated in Chapter 6 to be greater than 50 MHz in some cases. It can be assumed, then, that at best only a small fraction of the entire Doppler contour was saturated and that the probe laser resolution was probably not great enough to resolve the "hole" burned into the Doppler contour. Higher pump laser power and greater probe resolution are necessary for the success of this experiment.

The microwave experiment, on the other hand, does not suffer from wide probe frequency jitter or wide Doppler contours. Since the Doppler width of the probed 3LDR transition in this case is much smaller than the pressure broadening, any saturation of the infrared transition will
appear as a decrease in the total intensity of the microwave feature being probed. The experiment was also accomplished with a c.w. laser, thus making the experimental duty cycle much more efficient and signal to noise much greater than in the DILDOR experiment.

5.5 Improvements for future experiments

Several improvements in the existing apparatus could be made at minimal cost and effort. Firstly, a new grating for the monochrometer, one blazed for 10 μ operation, would boost the throughput of the device by a factor of 2 or 3. The grating currently in use is blazed at 3 μ and is working in third order.

Determination of the polarization of the diode beam can be easily done with a pile of plates polarizer. These plates can be Brewster angle salt windows, which are inexpensive and easy to handle.

Copropagating instead of counterpropagating beams might be a preferable geometric arrangement. Using copropagating beams, the pump laser is not aimed directly into the diode laser, and the effects of the pump laser on the probe laser mentioned in section 5.2 would be minimized. This arrangement will be discussed further in the following chapter.

Gross vibration of the diode laser itself can be minimized by using a very rigid mount instead of the rotatable
mount currently in use. Vibrations of the cold head caused by the 3 Hz motion of the displacer assembly it contains cause intensity (and probably frequency) fluctuations at the detector easily seen with lock-in detection.

Major improvements in design would require a larger investment. Specifically, a fraction of the probe beam should be split off for use as a measure of incident intensity for absorption spectra. In DILDOR scans this beam could be used to monitor the frequency of the probe by recording an appropriate reference spectrum simultaneously with the DILDOR spectrum. This would minimize the effects of scan-to-scan drift in the current tuning curve of the diode laser. This configuration, of course, necessitates the use of a second detector and phase sensitive detection electronics, as well as a good quality beam splitter. A multipen recorder would be necessary to record the detectors' responses simultaneously.

An electro-optic Q-switch for the pump laser would decrease pulse-to-pulse intensity variations and trigger jitter for the boxcar integrator. Electrical pickup from the high voltage pulses necessary to drive the device might be a major problem, however. Additional optical elements may be necessary to squeeze the resonator mode through the relatively small aperture of a currently available device. Pulse rates approaching a KHz could be realized, however, thus reducing the clock time required to recover a DILDOR spectrum by a factor of 3 or so.
The TDLS-II scanning current power supply should be replaced with a unit having much less hum in the diode laser current supply, if available.
6.1 Introduction

In the last chapter, the experimental results of two types of double resonance (DR), 2-level and 3-level, were reported. Spectra were recorded for pump powers ranging from 8.8 to 11.2 kW/cm^2, and, at the highest pump power, at different times during the 700 nsec long pump pulse. The spectra exhibited structure thousands of MHz from the CO\textsubscript{2} laser pump frequency, and the central feature grew broader with increasing pump power. From this, a rough estimate of the dipole matrix element was made; it was found to be in reasonable agreement with the theoretical estimate of Fox [6-1].

In both the 2-level and 3-level spectra, the satellite structure appeared to be asymmetrical around the pump frequency, showing more activity to the red of the pump. In fact, all absorption features within the J manifold of the most nearly resonant line showed activity. Since this activity appeared within the first 208 ns of the pump pulse, collisional relaxation was ruled out as the cause. Instead, an unspecified off-diagonal matrix element in the full SF\textsubscript{6} vibration-rotation Hamiltonian was invoked, which mixes the nearly degenerate ground state K levels (clusters) [6-8]. In this manner an entire J manifold could exhibit DR structure when only a few lines are directly pumped.
In this chapter, the assertions and conclusions mentioned above will be subjected to quantitative test. In particular, we will explore all terms in the molecular Hamiltonian capable of producing K state mixing, contemplate the effects of laser polarization, utilize the lineshape expressions of Mollow [6-2, 6-3] and of Hänsch and Toschek [6-4], include double resonance of the background hotband continuum, and reconsider the effects of collisions on the lineshapes reported in Appendix E.

6.2 Lineshape expressions

6.2.1 2-level spectra

For the moment we will ignore possible mixings between SF$_6$ cluster states and consider what lineshapes we would expect if the observed signals were merely a series of individual 2-level systems. The theory for these lineshapes is well understood; we will use the formalism of Mollow [6-2] which has been tested experimentally [6-3] by using a sodium beam as an ensemble of 2-level atoms.

Using the same notation of [6-2], the absorption lineshape $W'$ of probe beam is given by

$$ W'(\nu) = \frac{1}{2} \frac{\kappa (\kappa'^2 + \Delta \omega^2)}{\kappa' \Omega^2 + \kappa (\kappa'^2 + \Delta \omega^2)} \frac{AC + BD}{C^2 + D^2} \quad (6-1) $$

where

$$ A = \kappa \kappa' + \Delta \nu \Delta \omega - \Delta \nu^2 + \Delta \nu \Delta \omega \Omega^2 / 2 (\kappa'^2 + \Delta \omega^2) $$

$$ B = \kappa (\Delta \omega - \Delta \nu) - \Delta \nu \kappa' + \Omega^2 \Delta \nu \kappa' / 2 (\kappa'^2 + \Delta \omega^2) $$

$$ C = \kappa \kappa'^2 + \kappa (\Delta \omega^2 - \Delta \nu^2) + \kappa' (\Omega^2 - 2 \Delta \nu^2) $$

$$ D = \Delta \nu (\Delta \nu^2 - \Delta \omega^2 - 2 \kappa' \kappa - \kappa'^2 - \Omega^2) $$
In (6-1), $\Omega$ and $\Omega'$ are the Rabi frequencies for the pump and probe beams respectively, $\kappa$ and $\kappa'$ are the longitudinal and transverse relaxation rates respectively. The Doppler correction of (6-1) can be made by simply replacing the pump detuning $\Delta \omega$ and the probe detuning $\Delta \nu$ with

$$\Delta \nu + \Delta \nu (1 - \frac{v}{c})$$

$$\Delta \omega + \Delta \omega (1 + \frac{v}{c})$$

and numerically integrating over an appropriate distribution of molecular velocities:

$$W' = \int W'(\Delta \nu, \Delta \omega ; v) \exp(-mv^2/2kT) \, dv$$

Note that only a one-dimensional representation of the molecular velocities need be considered, that being along the axis of propagation common to both laser beams. In (6-2) the Doppler contributions are opposite in sign due to the counterpropagating geometry of the experiment.

Since the boxcar integrator is AC coupled, it actually integrates any difference in diode beam transmittance when the gate is open. That is, the signal is proportional to the amount of change in probe beam transmittance when the pump laser fires. Hence, to model our spectra, we must subtract from (6-3) the probe transmittance lineshape with no pump field present, which is simply a series of Voigt profiles.
Many authors [6-5] have studied three-level systems similar to ours. Because of its facile adaptation to this particular case, we will follow the method of Hänsch and Toschek [6-4].

We start from Eqn. (30) of [6-4] (which contains a typographical error not preserved here),

$$\chi = \frac{|p_{bc}|^2}{\pi} \frac{(\rho_{bb}-\rho_{cc})(\Delta_{ab}\Delta_{ac}+|\beta|^2)-(\rho_{aa}-\rho_{cc})|\beta|^2}{\Delta_{ab}\Delta_{bc}\Delta_{ac}-\Delta_{bc}^2|\beta|^2}$$

where $p_{jk}$ is the dipole matrix element between states $j$ and $k$, $\rho_{kk}$ is the diagonal Bloch matrix element for level $k$, and $\chi$ is the susceptibility. The remaining variables will be explained below. We can quickly make a few simplifying assumptions appropriate to our system: 1) all $\gamma_{ab}$, which are the relaxation rates of optical coherence, analogous to Mollow's $K'$, are equal; 2) all $\gamma_{a}$, the spontaneous decay rate of level $a$, are equal; 3) the probe is weak and strictly counterpropagating to the pump. Using these approximations, the probe absorption coefficient $\alpha$, analogous to Mollow's $W'$, can be expressed as

$$\alpha = \frac{\pi |k'| |p_{bc}|^2}{\pi} \frac{AR(\delta+\Delta\omega)\gamma'-B(R(\Delta\omega\gamma'-\gamma'\gamma')^2)-\beta^2(1-2R)}{A^2 + B^2}$$

where in this case $A = -\delta(\Delta\omega\Delta\omega+2\gamma'\gamma') - \Delta\omega\beta^2$; $W = \beta^2(2\gamma'/\Delta\omega^2+\gamma')$; $B = \gamma'(\delta^2-\beta^2-\Delta\omega\Delta\omega-\gamma')$; $\delta = \Delta\omega - \Delta s$; $R = 1 - \omega W/\gamma+2W$. 

6.2.2 3-level lineshapes
It may be useful to make the following correlations between Mollow's notation and that of (6-4)

\[
\begin{align*}
\Delta \omega & \leftrightarrow \Delta \omega \\
\Delta s & \leftrightarrow \Delta \nu \\
\alpha & \leftrightarrow \omega' \\
\beta & \leftrightarrow \Omega \\
\gamma & \leftrightarrow \kappa \\
\gamma' & \leftrightarrow \kappa'
\end{align*}
\]

Doppler broadening can be included by use of (6-3).

6.2.3 Broadening Mechanisms

Equations (6-4) and (6-1) give theoretical lineshapes for perfect beams. In practice, many dynamic imperfections are encountered, such as variation of probe intensity with frequency (PI), "instrumental" broadening (IB) of probe linewidth and frequency jitter caused by current supply hum and temperature wiggle, pump frequency jitter (PJ), and pump power variations during the boxcar gate (PP). PJ is at most the approximately 30 MHz width of the CO\textsubscript{2} laser gain profile, and will not drastically affect lineshapes hundreds of MHz away. Lines close to the pump will be totally saturated at the Rabi frequencies used, hence we will disregard PJ.

Since the absolute amount of DR signal is proportional to the incident probe intensity, the probe intensity profile was fitted to a convenient function of frequency. The shape of our diode laser mode peaked in the SF\textsubscript{6} P(29) manifold, which tended to accentuate lines to the blue of the pump frequency.
This function was included in the integration of (6-3). The apparent asymmetry of the 3LDR spectra is caused by the shape of the mode which drops severely in intensity to the blue of the main feature.

IB contributed by far the greatest source of broadening, although none of the factors contributing to this ad hoc effect were quantitatively known. It was assumed that the "perfect" spectra, including the absorption spectrum itself, could be averaged about a particular frequency \( \nu \) to find the observed signal at \( \nu \). The average was taken to be Gaussian about \( \nu \) with a variable width. The need for this broadening is apparent in Fig. 3 of Appendix E, wherein the observed linewidths are much broader than the Doppler width (26 MHz FWHM) at room temperature. For comparison to spectra shown below, an unbroadened 2-level spectrum is shown in Fig. 6-1.

Pump power fluctuations during the 0.5 \( \mu \)sec gate can be estimated from the contour of the laser pulse, which is shown in Fig. 6 of Appendix E. Spectra were calculated for the appropriate Rabi frequencies, and added together as an approximation to the integrating effect of the boxcar. As will be seen, PP proved to be a small effect.

6.2.4 Method of calculation

Each spectrum was calculated in a three step process. First, the absorption features in the diode laser mode were catalogued, and a single resonance spectrum calculated.
CALCULATED SF6 2-LEVEL DOUBLE RESONANCE

AC DR SIGNAL (ARB UNITS)

NU - NU(PUMP), MHZ

6.1. Calculated ZDR signal in SF6 using $\Omega = 230$, $K = K' = 3.8$, and Doppler width FWHM = 28 (all in MHz). No broadening has been included.
Absorption features near the CO₂ P(14) laser line were similarly catalogued from published spectra [6-7]. Next, lineshapes (6-3) were calculated using the Rabi frequency as a parameter. Finally, the difference or AC spectrum was broadened according to the methods outlined above. For the 2-level case, appropriately weighted hotband lines spaced every 10 MHz were included as an approximation to the continuous background absorption. The weighting of these lines was chosen so as to predict most closely the absorption spectrum at room temperature. A portion of the calculated absorption spectrum, which includes background lines and probe intensity correction, is shown in Fig. 6-2.

Calculations were accomplished in BASIC on a DEC MINC (LSI 11/2) computer at MIT (by CR), which required large stretches of calendar time, and independently in FORTRAN at Los Alamos (by Hal Galbraith). After a spectrum was calculated, it was scaled and compared to the digitized observed spectrum. In this manner a "best" set of parameters was found for both 2-level and 3-level calculations. Finally, worthy spectra were plotted on a Houston Instruments HIPL0T digital plotter. A typical MINC run required 14 hours to compute ten spectra.

The constants κ and κ' were taken to be equal in the strong collision limit. Patel and Slusher [6-6] have found that

\[ T'_2 = 22 \text{ nsec} \cdot \text{Torr} \equiv 1/\kappa' \quad (6-5) \]
6-2. Calculated SF₆ absorption spectrum near the CO₂ P(18) laser line at 945.9802 cm⁻¹. Background absorption has been included and 1B FWHM = 38 MHz.
from photon echo experiments in SF6. This agrees very well
with the observed time constant of the relaxation of the 2LDR
signal found in Appendix E, viz.:

\[ T = 23 \text{ nsec} \cdot \text{Torr} \equiv 1/k \equiv T_1 \]  
(6-5)
in the strong collision limit. At 0.08 Torr, we have

\[ k = k' = 3.6 \text{ MHz} \]  
(6-7)

6.3 Results

6.3.1 General features

Overall the DR lineshapes are dominated by two
conceptually different processes: AC Stark shifting and
saturation. When the pump laser is on, the apparent center of
a line not resonant with the pump is shifted away from the
pump frequency. This appears to be a "new"resonance, or an
upward deflection. The "old" resonance seems to disappear,
and hence produces a downward deflection. When added
together, the combination produces the derivative-like signals
apparent in Figs. 6-4 and 6-6.

Saturation occurs for lines relatively close to the pump
frequency. Since the Rabi frequency is much greater than the
Doppler width, entire lines can be saturated. The width of
the hole burned in the spectrum, however, is a complex
function of saturation and Stark shifting, so that the HWHM of
the hole is much larger than the Rabi frequency.
6-3. 2-level DR lineshapes for background hotband lines spaced 10 MHz apart. Outer curve, $\Omega = 140$; middle curve, $\Omega = 100$; inner curve, $\Omega = 95$ MHz. FWHM are 465, 285 and 235 MHz respectively. The slight baseline tilt reflects the observed hotband contour in this region.

6-4. Calculated 2LDR signal in SF$_6$ using $\Omega = 100$ MHz and 1B FWHM = 76 MHz (solid) and observed (dashed) for 11.7 kW/cm$^2$ at 0.08 Torr.
$U''$ FOR BACKGROUND (ARB UNITS)

PROBE DETUNING FROM PUMP, MHZ
DR SIGNAL (ARB. UNITS)

DETUNING FROM PUMP, MHZ
6-5. Average square deviation of calculated 2-level spectrum from observed. Rabi frequencies \( \Omega \) are \( \circ = 80; \ \Delta = 95; \ \Delta = 100; \ \bullet = 105 \). PI corrections and background absorption are included in these computations.
This is demonstrated in Fig. 6-3 for the "continuous" background lines. Since the lines are very dense, there is no structure far from the pump frequency where a Stark shifted resonance conceals the disappearance of a "no field" resonance. Only the saturated "hole" appears, which is symmetrical around the pump frequency.

6.3.2 Specific spectra

The closest fit to the observed 2LDR spectrum taken at 11.7 kW/cm² is shown in Fig. 6-4. Parameters used in its computation are $\Omega = 100$ MHz and IB FWHM = 76 MHz. The average square difference (SS) between the scaled calculated spectra and the observed spectrum are shown in Fig. 6-5; the SS minimized slowly around the values quoted above. PP broadening was not included due to its high computational overhead.

Similar plots for the 3LDR experiment are shown in Figs. 6-6 and 6-7. The fit of 3-level spectra is more strongly dependent on IB, and less on $\beta$ than for the 2-level fit. In this case, best values correspond to $\beta = 65$ MHz and IB FWHM = 120 MHz. When PP broadening was included, the SS was not improved but a slightly lower IB (110 MHz) was needed for best fit. Values of SS for the PP broadening are nearly identical to those for $\beta = 65$ MHz. Rabi frequencies were mixed according to the profile of the average pump laser profile, 51:65:71:78::0.3:0.3:0.2:0.2.
6-6. Calculated 3LDR signal in SF₆ using β = 65 MHz and 18 FWHM = 120 MHz (solid) and observed (dashed) at 0.08 Torr.
6-7. Average square deviation of calculated 3-level spectra from observed. Rabi frequencies $\hat{\beta}$ are $\circ = 51; \, \, + = 65; \, \, \Delta = 75; \, \, \bullet = 90; \, \, \bigtriangleup = 100$. PI correction is included.
6.4 Discussion

6.4.1 Parameters

As can be seen in Figs. 6-4 and 6-6, the fit is surprisingly good for a two parameter calculation. All deflections are accounted for, excepting baseline drift of the boxcar. Deflections are caused primarily by Stark shifted resonances. The main features in both spectra, caused by saturation of a few transitions, are fit very well.

The parameter \( \Omega = \beta \) (Rabi frequency) can be calculated from theoretical estimates [6-1] of \( \mu_1 \) and the measured average intensity of the pump laser. It is important to correct the dipole moment of [6-1] for interaction with a polarized beam in a rotating-wave formalism, so that

\[
\Omega = \beta = \frac{\mu \cdot \mathbf{E}}{2\hbar \gamma} ; \quad \mu = 0.388 \times 10^{-18} \text{ esu} \cdot \text{cm} \quad (6-8)
\]

Using measured values of the average pump power, beam diameter, repetition rate and pulse width, we can estimate \( \Omega \) to be 81 MHz for the 2LDR experiment and 72 MHz for the 3LDR case (a slightly lower pump pulse power was used for 3LDR). The value for the 3LDR experiment is within 10% of the value used in the "best" computation; the error in its calculation from four experimentally determined quantities certainly exceeds this figure. Furthermore, since the minimum of SS is so shallow, the difference in SS for \( \beta = 65 \) and \( \beta = 72 \) is
merely a few percent. The error in digitization of the
observed spectrum is certainly of comparable size. Hence, it
can be confidently concluded that the two estimates of $B$ are
not significantly different in this case.

The Rabi frequency calculated for the 2LDR experiment is
decidedly low, perhaps as a result of the method used to
choose which calculated spectrum represents the best fit or
shot to shot variations in the pump laser intensity. As was
mentioned above, PP broadening was not extensively studied for
the 2-level system. It does not, however, mitigate the
conclusion that the theoretical estimate of $\mu$ is accurate
to within 25%.

The values of IB required to fit the spectra exceed the
apparent IB in the absorption spectra taken with this
apparatus, which in turn is larger than that of other
experiments [6-7]. It must be ascribed to electronics and
technique unique to this experiment. For instance, scattered
pump laser light may cause temperature fluctuations or optical
pumping in the diode laser. Crossed laser beams would
alleviate this problem, but the added effort in analyzing a
two dimensional Doppler profile would be considerable. It may
be noted that copropagating beams would produce somewhat
narrower features [6-3] than counterpropagating beams.

The apparent need for different values of IB is also
somewhat puzzling, although many possible explanations exist.
Since the two experiments were performed in different regions
of the diode laser mode, one would expect different tuning rates per unit current $d\nu/dI$ and per degree $d\nu/dK$. The probe frequency jitter would not be equal at different frequencies in the same mode if hum and temperature jitter remain constant. Furthermore, there is no guarantee that on a particular day the diode laser was completely occluded from the pump beam, since the alignment of the pump beam was constantly tweaked. Small amounts of pump light leaking into the diode laser assembly would contribute to an apparent frequency jitter. A copropagating geometry would be less prone to these effects. Again, since the minimum in SS for 2-level fit is so shallow, the value of SS for the 2-level fit for $N=100$ at $IB=120$ (the same as for minimum SS for the 3-level fit) is only 4% larger than for $IB=76$. Digitization errors may well account for this difference.

6.4.2 Off-resonant pumping

A look at features to the red of the main 2LDR signal shows that the observed signals are considerably larger than those calculated here. It is tempting to ascribe this discrepancy to mixings via the molecular V-R Hamiltonian, but as is shown in Appendix H, there are no mixings sufficient to cause the added signal intensities. By default the only other processes capable of causing the effect are experimental artifacts (such as $\nu$-dependent IB) and collisions. The repeatability and excellent signal to noise of the experiments tends to deny the importance of the former process.
In Appendix E it was concluded that since the satellite structure in the 2LDR spectra was fully developed within the first 200 ns of the pump pulse, the structure was not caused by collisional relaxation. This conclusion may have been hasty, especially in light of the apparent lack of mixings via the molecular Hamiltonian. A collisional process operative on such a short time scale implies a cross section of about 600 \( \text{A}^2 \), which is at least three times larger than that for longitudinal (and transverse) relaxation. This is certainly a large figure, especially for a collisional process such as \( M \)-changing collisions [6.8a].

Changing the orientation of the lab-fixed component of the average dipole moment during a polarized pump laser pulse would tend to increase the unsaturated DR signals if the polarization of the probe were at right angles [6-8]. Since the polarization of the (now dead) particular diode was not determined, and in general is not known for these devices, a definitive statement cannot be made on the effects of relative polarization in this case. Double resonance experiments currently underway using lower temperatures and different geometries with a new diode laser may shed some light on this problem.
In this chapter, the results and conclusions obtained in Chapters 2 through 6 are summarized.

7.1 Laser induced chemistry

1) No entirely new reactions were observed; all LID reactions reported here have been accomplished by other methods. No mode-specific or mode-selective reactions were seen, although efforts to find reactions and conditions which might lead to mode selectivity are continuing.

2) RRKM unimolecular reaction rate theory has been used to describe the observed data quantitatively. Since the RRKM formalism is based on the assumption that energy within the molecule is distributed statistically amongst all the vibrational modes, the success of RRKM theory implies that for the conditions of these experiments (and those of many other experiments), energy absorbed from the laser field is randomized before a molecule dissociates. Thus we have an indirect answer to Question (2) of Chapter 1 (How does the energy distribute?), at least in part; apparently energy flows into all molecular modes.

More precise details, such as the role of collisions, intramolecular anharmonic, Coriolis and Fermi couplings of
modes, and field-induced effects are not elucidated by chemical evidence. The ability to perform LID in a molecular beam implies that collisions are not necessary for the absorption of an amount of energy sufficient for reaction. It must be stressed, however, that the distribution of absorbed energy amongst vibrational modes in a MIRPA experiment has not been directly probed experimentally in beam or in bulk conditions. Although research interest in this area continues, more direct answers to Question (2) than the above statement cannot be made before new spectroscopic evidence is obtained.

3) The distribution of molecules over energy has not been determined. To ascertain the true shape of the distribution of molecular energies, an appropriate spectroscopic technique is required which interrogates individual molecules undergoing MIRPA. Projects such as that begun by Burak and Quelly [7.1] and currently being extended by Mark Spencer may provide some insight.

4) Other important dynamical effects, such as the effect of the laser pulse shape on energy deposition and the effects of collisional deactivation, have not been explored in great detail. Some evidence of the time scale over which deactivation can become significant has been obtained by LID experiments done with buffer gases. In the LID of trans-dichloroethylene, for example, the presence of a few percent of the nonabsorbing "cold" cis isomer was sufficient
to quench the absorbing "hot" trans isomer before dissociation could occur. Since the TEA laser pulse has a nominal FWHM of 70 ns, the deactivation rate must be a very fast process in this example. Data of a more quantitative nature would be difficult to obtain by bulk chemistry experiments.

5) Despite the lack of dynamical information, we have shown that the chemistry produced by MIRPA can be controlled by various experimental parameters, such as pressure, focal geometry and choice of buffer gas. Proper choice can produce very selective results; for example, in the LID of CF₂CHCl, CF₂CH₂ was produced in preference to other products when hydrogen-containing buffer gas was added. By choosing a suitable parent molecule, a particularly valuable radical can be produced in large local concentrations. The astute selection of parent molecule together with appropriate experimental conditions has allowed a degree of control over the production of many transient species which cannot be had by other means [1.13].

6) Evidence reported in Chapters 2 and 3 and in Appendix B shows that the vinylidene carbene F₂C=C: has been produced by LID. Evidence for the formation of the dimethyl analog, (CH₃)₂C=C:, is not as convincing. This may be a suitable method of producing vinylidene carbenes for spectroscopic investigation of their electronic structure.

7) Radicals produced by LID are born with some vibrational energy, which in the cases of (CH₃)₂C=C: and
H₂C=C: is sufficient to overcome the energy barrier to rearrangement. The observation of "hot" fragments is in concert with the data of other investigators [1.12,7.2].

### 7.2 Gaussian beam optics

8) It is possible to determine the average of an intensity-dependent effect, such as the average energy absorbed per molecule $\langle E \rangle$, for a small volume of species at the center of a Gaussian laser beam. This technique, Gaussian beam deconvolution, may be valuable in determining the energy centroid of the distribution discussed in (3) above. The effectiveness of the method is limited ultimately by the precision of the experimental measurements, as was shown in Chapter 4.

9) Subjecting a sample to the very wide range of fluences incurred in a focused Gaussian beam geometry tends to make the dispersion of any observed quantity look Gaussian also. This is demonstrated graphically in Fig. 3 of Appendix D. Mechanistically this effect is easily understood: the effective "dispersion" of fluences experienced by molecules in the focused beam is so much wider than the dispersion of the energy absorption function incurred at each point in the beam (that is, the width of the distribution of molecules over absorbed energy at a given fluence $P(E; \phi)$), that the geometric beam "dispersion" swamps the effect of distributions $P(E; \phi)$. This implies that observed quantities which are
averaged over the entire beam will be more sensitive to
to macroscopic beam shape than the microscopic dynamics of the
physical process. The chemical data on the LID of
trans-\(\text{d}_1\)-vinyl chloride versus focal length, depicted in Fig.
2 of Appendix A, are a striking example of this effect. In
this case, the total molecular behavior was seen to be
strongly dependent on beam geometry and independent of the
form of distribution \(P(E; \phi)\) used to model the data.

7.3 Double resonance experiments

From the modeling of 2LDR and 3LDR spectra in SF,
several conclusions can be made.

10) The value of the dipole matrix element \(\mu\) has been
estimated accurately.

11) It was convincingly shown in Appendix H that mixings
between cluster states within the same \(J\) level caused by the
full vibration-rotation molecular Hamiltonian do not play a
significant role in the observed 2LDR and 3LDR spectra.

12) Lineshape equations derived from two and three level
Bloch equations describe individual features very accurately.
An excellent fit for all features is precluded by the
exclusion of collisional effects.

13) To a first approximation, however, the observed
spectra can be modeled as a set of independent 2-level and
3-level systems. The dynamics of collisional coupling between
states in the same $J$ manifold is currently under consideration by Harold Galbraith at Los Alamos. Collisions may cause population to be transferred to or from $K$ states within the $J$ manifold being directly pumped, and would be observed as a corresponding increase or decrease in the double resonance signals detected for these $K$ states. This effect may be difficult to separate from the effects of AC Stark shifting, instrumental broadening and observation times long compared to the rate of collisional relaxation.

14) As a test of the hypothesis that collisions are playing a role in the observed spectra, the double resonance experiments should be repeated in SF$_6$ at low temperatures. At 140 K, the lowest temperature practical with SF$_6$, collisional relaxation rates would be decreased by a factor of $\sim \sqrt{2}$ from their room temperature values. Since a greater fraction of the molecules are in the ground vibrational state at 140 K, a decrease in number density might be affordable with no loss of signal, further decreasing the collision rate. Also, other apparent anomalies, such as the instrumental broadening, could be investigated.

15) The use of a tunable diode laser as a probe source has been an invaluable tool, enabling us to record spectroscopic details not observable by using fixed frequency probe radiation. Improvements in diode laser stability and effective linewidth must be made so that the observed instrumental broadening ceases to be the limiting factor in
the resolution of the double resonance spectra. Some suggestions to this end were put forth in Chapter 5.
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APPENDIX A. "Infrared Photochemistry of Halogenated Ethylenes"


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Infrared Photochemistry of Halogenated Ethylenes

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Abstract: The infrared laser induced multiphoton reactions of mono-, di-, and trichloro-substituted ethylenes have been investigated. In all cases, the dominant mode of reaction is elimination of HCl. Free rotation around the double bond precedes elimination, leading to observation. In the cases of 1,2-dichloroethylene and 2,3-dichloroethylene, the experimental results can be represented in terms of a single mode of excitation calculated from RRKM theory, which presupposes unimolecular elimination of vibrational energy within the molecule prior to reaction. Comparison of HCl/DCI elimination ratios between CHD=CHCl and CHD=CHDCI shows that the preferred mode of elimination is to the chlorine atom. The pressure dependence of this product ratio is the same for different CO laser lines, however, this ability to influence the outcome of the reaction by changing the laser line is a consequence of differences in energy deposition between one line and another, and not of any mode-selective process. The preference for elimination suggests that the reaction may proceed by formation of vinylidenes, followed by rearrangement to form acetylene.

Since the first published report of the dissociation of SF₆ by infrared multiphoton absorption,¹ chemical reactions induced by high-intensity infrared radiation have captured the imagination of a large number of both chemists and physicists. A principal reason for this interest is the apparent substantial difference between the conditions under which such reactions occur and those of normal thermal-equilibrium conditions. In the latter, molecular internal (vibrational) and external (translation/rotational) degrees of freedom are in mutual thermal equilibrium, or close to it, while in reactions resulting from multiphoton infrared absorption, the energy required to activate the reaction channel is, at least initially, deposited exclusively in the vibrational modes. There has even been speculation that energy could be preferentially localized in one or a few vibrational modes, thereby leading to chemical transformations which are qualitatively different from those observed under conventional conditions. In the experiments reported in this paper, we have studied a series of mono-, di-, and trichloro-substituted ethylenes in order to shed some light on the extent to which nonequilibrium effects may be reflected in overall chemical behavior.

An extensive literature has developed on these reactions in the past 2 years, which is summarized in several reviews.² Most of the reactions studied involve homolytic bond cleavage, as in SF₆, SF₅CN, CH₃COCH₃, and similar systems. More recently, interest has turned increasingly to the types of reactions familiar from conventional thermal chemistry, but carried out under nonequilibrium excitation conditions. Typical examples include elimination of hydrogen halides:¹ ²

$$\text{CF}_{3} \rightarrow \text{F} + \text{CF}_{2} \rightarrow \text{CH}_{2} = \text{CH}_{2} + \text{HF} \quad (1a)$$

$$\text{CF}_{9} \rightarrow \text{F} + \text{CF}_{8} \rightarrow \text{CH}_{2} = \text{CH}_{2} + 2 \text{HF} \quad (1b)$$

More complex dissociation/isomerization pathways have also been identified as having an origin in specific vibrational excitation, such as eq 6. Reactions 1a and 5, in particular, have

$$\text{CH}_{2} = \text{CHBr} + \text{HBr} \rightarrow \text{CH}_{2} = \text{CHBr} \quad (2)$$

condensation to form aromatic rings² (eq 4).

$$\text{CH}_{2} = \text{CHCl} + \text{HBr} \rightarrow \text{CH}_{2} = \text{CHBr} \quad (4)$$

and cyclic ester pyrolysis² (eq 5).

$$\text{CH}_{2} = \text{CHCOOCH}_{2} \rightarrow \text{CH}_{2} = \text{CHCOOCH}_{2} \rightarrow \text{CH}_{2} = \text{CHBr} \quad (5)$$

The attractive feature of this series of molecules is that the primary laser-induced process is a simple HCl elimination.³ There are also competitive channels present (such as isomerization or C-Cl bond cleavage) which provide quantitative tests of models of the dynamics of the process. The formation of stable molecular fragments, rather than reactive radicals or atoms, also simplifies the overall kinetics by avoiding secondary reactions. The reactions of the different members of the series provide information on the mechanism and stereochemistry involved, and a sufficient background on conventional thermal reactions of these species exists so that a meaningful comparison may be made between laser- and thermally induced processes. Furthermore, the vibrational spectroscopy of the parent molecules is well characterized, so that quantitative estimates may be made of energy deposition, densities of states, and other parameters required in a detailed theoretical treatment.

Experimental Section

Irradiation System. The infrared source was a Toshiba 25G CO₂ laser furnishing 0.1-1.0 J pulses on times of the P and R branches of
the 9.6 and 10.6-um bands. Each pulse consisted of a 40-50 um spike containing over 70% of the energy focused by a much lower intensity laser. Transient mode operation was constrained to 1 Hz. Followed by semiconductor diodes. The beam was focused in the reaction mixture by a 7.1 cm lens. Argon laser line 29.0 cm. 9.6 for convenience. A two-lens telescope was used consisting of a pair of 25-cm coated Ge lenses giving effective apertures between 7.6 and 4.7. 700 um. 16 to 7.6 cm. 30 to 111 cm. were chosen so as to match the small gap between Nipkow disks. Care was taken to focus the beam so that there was no overlap between the disks. The net concentration of ethylenic radicals with the acetylene radical was used to achieve the desired overall reaction, as well as a photon density of 99%. Based on attempts at poor yield. The resulting products tend to be unstable. To control the mixture containing C:C-I. formed in reaction 10 appears to be stable over an extended period; the CCI diode finally exploded after repeated transfer, presumably because of leakage of O-throme into the cell.

The CCI-HCl observed in the infrared photolysis of IV may have been formed by a-C-elimination or a-C-elimination of CCI.

\[ \text{CHCl} + \text{HCl} \rightarrow \text{CCI} + \text{HCl} \quad (11) \]

Our experiments cannot distinguish between these two channels for this molecule. The lack of CCI among the infrared photolysis products of II indicates that a-C-elimination has not occurred for that system. Furthermore, the absence of thermal addition products, especially CCl/CHCl, in the reaction mixture indicates that CCl elimination is not a major pathway. Steinfeld et al.\(^5\) report that IV fragments to CCl and Cl atoms in a beam of the parent molecules. Such a process may be visible in the photolysis of CCl/CHCl mixtures. Again, our experiments may not show products other than those of molecular elimination. Presumably, at high fluences and low pressures used by Gandini or Sudbo, the vibrational energy content of the molecule is driven to much higher levels than in our experiments. \(^{24-25}\) We note that the thermal pyrolysis of I between 385 and 445 °C results in condensation to hexachlorobenzene, \(^{24-25}\) a reaction reminiscent of the laser-induced process in tetrafluoroethylene. BCI mixtures:

\[ \text{C}_2\text{H}_4 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_2 + \text{HCl} + \text{Cl} \]
C. trans-Dichloroacetylene. When 1 Torr of HCl is irradiated with the P(30) [10.6 μm] line of the CO₂ laser, the principal reaction product is trans-dichloroethylene. Very little elimination product (HCl + CH₂Cl₂ or HCl + HCl₂) is observed. This result is in agreement with that found by Ambartzumian et al. 26 Nagas and Kataoka,27 and also Kashi and Zare; 28 who reported that trans-dichloroethylene is the principal laser-induced reaction path in this system. This process is also the principal thermal reaction in the system, with an activation energy of 55 kcal mol⁻¹, a small amount of condensation to 1,2,4-trichlorobenzene is also reported, 21 which is not found in the laser-irradiated samples.

In interpreting this result, it is important to remember that measurements of product formation are made following a large number (200-2000) of infrared pulses. Initially, both isomerization and dissociation may take place (see following section), but as the irradiation proceeds, an appreciable concentration of cis-dichloroethylene accumulates in the cell. This species does not absorb CO₂ laser radiation, so that vibrationally excited trans species is progressively diluted by cold cis molecules. Under the conditions of the experiment, this leads to rapid deactivation of the trans molecules, so that the higher energy HCl elimination channel (E₁') is quenched while the lower energy dissociation channel (E₂') is still able to proceed. This point is discussed in more detail in the following section.

D. α-d₁ and trans-d₁-Vinyl Chloride (α₁β). In order to investigate the laser-induced elimination reaction in more detail, α-d₁- and trans-d₁-vinyl chloride were synthesized as described above and subjected to infrared photolyzing conditions. The resulting reactions were, for the α-d₁ species:

\[ CHD = CHCl + hν \rightarrow CHD + Cl \]  (12a)

while the trans-d₁ initially isomerized (eq 13)

\[ D_2 \quad D_2 \quad \text{(eq 13)} \]

and subsequently eliminated to form acetylene (eq 14).

\[ CHD = CHCl + hν \rightarrow CHD + Cl \]  (14a)

The product mixtures from all reactions were carefully examined for evidence of deuteration migration, but none was found, that is, no cis or trans d₁-d₂ species was formed when starting with the α-d₁- and no α-d₁-d₂ was formed when starting with trans-d₁.

A diffusion experiment was also carried out on a 1:1 mixture of α-d₁- and H₂-vinyl chloride. The latter component was excited by infrared radiation from the 9.66 μm band of the CO₂ laser, which is not adsorbed by, and thus deuterated species. The dissociation yield was considerably r:; from that expected from pure vinyl chloride at the same pressure. This is attributed to rapid vibrational deactivation by the unreacted trans-d₁ species present in the mixture. Similar behavior was seen in the trans-dichloroethylene system, which isomerizes to the nonabsorbing cis form. In a mixture in which both species are excited by a given infrared laser frequency, such as the trans- and cis-d₁-vinyl chloride discussed below, there was appreciable deactivation of the reaction yield.

Elimination Ratio and HCl/ClD Elimination. One question we wished to explore was whether there was any preference for elimination from a particular position in the parent molecule, i.e., the branching ratios for reactions 12 and 14. This was investigated by measuring [C₆H₁₂]/[C₆H₁₃] ratios in the products of these reactions, using GC/MS. In order to make sure that the measured isotope ratios indeed reflected the initial branching ratio, and were not affected by subsequent H atom exchange, a mixture of C₆H₆ (Merck Sharpe and Dohme) started deuterium purity >99% and HCl was analyzed over a 9-day period. This experiment demonstrated that the absence of d₁-vinyl chloride in the infrared spectrum of the mixture showed that back reaction between acetylene and HCl was negligible under our conditions. (2) The infrared spectrum of the acetylene showed that C₆H₆ made up less than 5% of the total, verifying that H/D exchange also did not occur.

The results of the experiments are shown in Figure 1. As will be discussed shortly, cis-trans isomerization precedes HCl elimination in CHD = CHCl. Thus, the preponderance of HCl (ν = DCI) elimination in that system could be consistent with either cis, trans, or even elimination. But the opposite result in CHD = CCl₃ coupled with the lack of H migration across the double bond, can be explained only by strongly favored D or α-d₁ elimination.

The HCl/DCI elimination branching ratio also displays an interesting dependence on reactant pressure and laser line, as shown in Figure 1. For irradiation by the P(30) line, this ratio is nearly constant with pressure (~80% HCl elimination from CHD = CHCl, ~90% from CHD = CCl₃). With the P(31) line, however, the HCl elimination ratio from CHD = CHCl drops from ~80% to ~65% over the pressure range 0.3-1.5 Torr. Several possible explanations for this behavior may be considered.

(1) The elimination of HCl or DCl from a particular site may be specific to the mode excited by the laser, with mode specificity relaxed by collisions. This is considered particularly unlikely for several reasons. First, the two laser lines (P(30) and P(31)) excite different rotational states of the same mode of vibration in the CHD = CHCl molecule. Furthermore, all other behavior of this bond and many other systems is best interpreted in terms of rapid redistribution of vibrational energy within the molecule, rather than by mode-specific excitation.

(2) Some bimolecular process, such as H atom abstraction,
may tend to make different sites equivalent. Since no radical chain products are found in any of the reaction mixtures, however, this is also considered unlikely. Furthermore, such a mechanism would not be sensitive to which laser line was used to excite the system.

(3) The most plausible explanation is in terms of competing unimolecular elimination pathways for \( \text{cis-} \) and \( \text{trans-} \) vinyl chloride, with very similar threshold energy for the two modes of dissociation, as in the case of \( \text{HX} \) elimination from haloalkanes. Energy deposition studies show that more energy is coupled into the vinyl chloride at higher pressures, leading to different average vibrational excitations. The energy deposition is strongly dependent on which laser line is used. This will be discussed in greater detail in the following section.

**Competence between Reaction Pathways: Isomerization vs. Elimination.** As noted above, infrared irradiation of \( \text{trans-} \) vinyl chloride always produced substantial quantities of the \( \text{cis} \) isomer along with dissociation products. In order to get, in information about the competition between the isomerization pathway (reaction 13) and the elimination reaction 14, a series of experiments was carried out at varying energy fluences through the sample. This was done by condensing the CO laser beam with the two-Gem-lens telescope, which has the number variable between \( f/20 \) and \( f/70 \). A simple treatment of the geometrical optics of the lens system gives, as a first approximation to the peak intensity at the focal point of the beam,

\[ I_{\text{peak}} = \frac{P_r}{\pi D^2} \]

where \( P \) is the peak power of the laser pulse (\( 6.7 \times 10^8 \) W) and \( \lambda \) the wavelength (1033 nm). Thus the intensity at the focal point varied between \( 3.5 \times 10^9 \) W/cm\(^2\) (at \( f/70 \)) and \( 4 \times 10^9 \) W/cm\(^2\) (at \( f/20 \)).

The results are shown in Figure 2. At large \( f/\) numbers (weak focusing), no HCl or acetylene is produced, and the \( \text{cis-} \) \( \text{trans-} \) ratio remains at its initial value. As the focusing is increased, isomerization is seen to take place while relatively little dissociation occurs. At the lower \( f/\) number optics used, the isomerization appears to level off at a \( \text{cis-} \) \( \text{trans-} \) ratio of about \( 1.2 \), while extensive dissociation occurs. The equilibrium ratio of the two isomers, calculated as the ratio of vibrational partition functions, was computed to be 0.92 at 300 K and 0.95 at temperatures exceeding 600 K. The somewhat larger experimental value may reflect preferential absorption of the infrared radiation by the trans isomer relative to the cis, leading to a greater degree of dissociation.

The basis of this behavior is the lower activation energy for isomerization relative to HCl elimination. This leads to the possibility of the former reaction taking place at lower vibrational energy content in the vinyl chloride molecule than is required for dissociation.

**Comparison with RRKM Theory.** A kinetic Model. Most detailed treatments of multiphoton induced reactions\(^{10}\) have relied on the assumption that the equation incorporating the partition function for the population over energy, \( f(E) \): (a) The average energy \( \left\langle E \right\rangle \) of the distribution increases only during the laser pulse. (b) A maximum \( \left\langle E \right\rangle \) is reached during the pulse where up pumping is balanced by population loss via reaction of hot molecules. (c) Very little reaction occurs after the pulse because molecules unreacted by the end of the pulse are collisionally deactivated. (d) The shape of the population distribution is nearly identical with a Poisson for \( \left\langle E \right\rangle \) below the critical energy of reaction. To avoid the lengthy computation and the numerical approximation, \( f(E) \) was used to obtain the individual rate coefficients coupling the various energy levels, we have used these observations as the basis of a simplified kinetic model.

\[ f(n) = \frac{e^{-\gamma}(\gamma/n)^n}{n!} \]

with \( E = nh\nu \) and \( (\gamma) = (\nu)h\nu \). Although the master equation treatments predict a Poisson, this may be an artifact of using a harmonic energy grid, thus producing the same distribution as for coherently pumped harmonic oscillators. The broadest distribution possible is the maximal entropy or Boltzmann-like distribution\(^{16}\)

\[ f(E) = \frac{N(E) e^{-\gamma E}}{Q} \]

where \( N(E) \) is the Whittaker-Rabinovich expression for the density of states.\(^{10}\)

\[ Q = \int_0^\infty N(E) e^{-\gamma E} dE \]

and \( \gamma \) is a temperature-like parameter determined from

\[ (E) = \int_0^\infty EN(E) e^{-\gamma E} dE \]

(b) When reaction occurs, the form of the distribution is not greatly affected. For the 3.2 Torr \text{-} \text{vinyl} chloride system used in this model, very little reaction occurs for each pulse. Only the highest energy molecules, comprising a small fraction of the total distribution, react.

(c) In the 6-s interval between laser shots, the products from the reaction zone mix by diffusion, into the rest of the unreacted cell volume.

(d) Using assumptions (a)–(c), the net reaction can be approximated by a continuous process analogous to placing all the brief intervals of reaction back to back. The total time of reaction is then the total number of laser pulses times the reaction time per pulse. This time was chosen as \( 10^{-11} \) s pulse, to include the full laser pulse and to allow for two or three collisions (at 3.2 Torr) during each pulse.

(e) Since the \( (E) \) of the population distribution is state-dependent (b) during this interval, a constant reaction rate for a particular reaction \( i \) can be calculated using RRKM unimolecular reaction rates averaged over the proper population distribution.
\[
\rho = \frac{g^a}{k^f} = \frac{k^f}{p^f + r^f}
\]

The total reaction time was 1.5 \times 10^{-4} s, as mentioned above.

The coefficients \(c_1\) and \(c_2\) are found from the initial conditions, \(\{\text{trans-}d_1\}\) at 0, where \(c_1 + c_2 = 0.78\) for the sample we used, and

\[
\{\text{cis-}d_1\}\}_{t=0} = c_1 \gamma^+ + c_2 \gamma^-= 0.22
\]
and solutions learning the precursor concentration \( E \).

\[ \frac{\text{d}[C(H)]}{\text{d}t} = -k_1 [C(H)] + \text{rate} \]

\[ \text{rate} = \text{constant} \times [A] \]

\[ \text{rate} = k_2 [C(H)] + k_{ld} [C(H)] \]

\[ k_{ld} = k_{ld1} + k_{ld2} \]

\[ k_2 = k_{2a} + k_{2b} \]

\[ k_{ld1} = k_{ld1a} + k_{ld1b} \]

\[ k_{ld2} = k_{ld2a} + k_{ld2b} \]

\[ k_{ld1a} = k_{ld1a1} + k_{ld1a2} \]

\[ k_{ld1b} = k_{ld1b1} + k_{ld1b2} \]

\[ k_{ld2a} = k_{ld2a1} + k_{ld2a2} \]

\[ k_{ld2b} = k_{ld2b1} + k_{ld2b2} \]

\[ k_{ld1a1} = k_{ld1a11} + k_{ld1a12} \]

\[ k_{ld1a2} = k_{ld1a21} + k_{ld1a22} \]

\[ k_{ld1b1} = k_{ld1b11} + k_{ld1b12} \]

\[ k_{ld1b2} = k_{ld1b21} + k_{ld1b22} \]

\[ k_{ld2a1} = k_{ld2a11} + k_{ld2a12} \]

\[ k_{ld2a2} = k_{ld2a21} + k_{ld2a22} \]

\[ k_{ld2b1} = k_{ld2b11} + k_{ld2b12} \]

\[ k_{ld2b2} = k_{ld2b21} + k_{ld2b22} \]

\[ k_{ld1a11} = k_{ld1a111} + k_{ld1a112} \]

\[ k_{ld1a12} = k_{ld1a121} + k_{ld1a122} \]

\[ k_{ld1a21} = k_{ld1a211} + k_{ld1a212} \]

\[ k_{ld1a22} = k_{ld1a221} + k_{ld1a222} \]

\[ k_{ld1b11} = k_{ld1b111} + k_{ld1b112} \]

\[ k_{ld1b12} = k_{ld1b121} + k_{ld1b122} \]

\[ k_{ld1b21} = k_{ld1b211} + k_{ld1b212} \]

\[ k_{ld1b22} = k_{ld1b221} + k_{ld1b222} \]

\[ k_{ld2a11} = k_{ld2a111} + k_{ld2a112} \]

\[ k_{ld2a12} = k_{ld2a121} + k_{ld2a122} \]

\[ k_{ld2a21} = k_{ld2a211} + k_{ld2a212} \]

\[ k_{ld2a22} = k_{ld2a221} + k_{ld2a222} \]

\[ k_{ld2b11} = k_{ld2b111} + k_{ld2b112} \]

\[ k_{ld2b12} = k_{ld2b121} + k_{ld2b122} \]

\[ k_{ld2b21} = k_{ld2b211} + k_{ld2b212} \]

\[ k_{ld2b22} = k_{ld2b221} + k_{ld2b222} \]

\[ k_{ld1a111} = k_{ld1a1111} + k_{ld1a1112} \]

\[ k_{ld1a112} = k_{ld1a1121} + k_{ld1a1122} \]

\[ k_{ld1a121} = k_{ld1a1211} + k_{ld1a1212} \]

\[ k_{ld1a122} = k_{ld1a1221} + k_{ld1a1222} \]

\[ k_{ld1b111} = k_{ld1b1111} + k_{ld1b1112} \]

\[ k_{ld1b112} = k_{ld1b1121} + k_{ld1b1122} \]

\[ k_{ld1b121} = k_{ld1b1211} + k_{ld1b1212} \]

\[ k_{ld1b122} = k_{ld1b1221} + k_{ld1b1222} \]

\[ k_{ld1b211} = k_{ld1b2111} + k_{ld1b2112} \]

\[ k_{ld1b212} = k_{ld1b2121} + k_{ld1b2122} \]

\[ k_{ld1b221} = k_{ld1b2211} + k_{ld1b2212} \]

\[ k_{ld1b222} = k_{ld1b2221} + k_{ld1b2222} \]
the RRKM rate theory described in the preceding section, with the experimental data for each limiting form of the vibrational energy distributions, and at various flux conditions. The rate constant (determined from the integral over all fluxes, or denoting probability distribution) is given by the proper percent dissociation of the reactant (i.e., triatomic acetylene and HC1). This value was then used to calculate the expected [C] ([C]) ratio at a given energy flux.

As can be seen from Figure 4, either form of the distribution is capable of reproducing the observed [C] ratio. The differences is that at any given flux, the value of [C] which is recovered is twice as high for the narrower 

fraction function (eq 16) than for the maximal counting rate distribution (eq 17). This is a result which would be expected from the observed [C] ratio at the energy flux.

We also tested the effect of small variations in the activation energy. For the numerator and two dissociation channels with the same experimental uncertainties for these quantities (eq 17) the value listed in the current figures 3 and 4 give the best agreement with the data. The effect of allowing a small amount of differential excitation between cis and trans molecules is also shown in Figure 5, increasing [C] (eq 17) from zero to twice the observed value; the former ratio decreases, and the latter increases, as the mean excitation (E) of the system is raised. This (E) dependence could explain the pressure dependence found in the P(38) line increasing vinyl chloride pressure often has the effect of decreasing the mean excitation of the molecules, since pressure broadening of the absorption lines helps to overcome local saturation effects. The magnitude of this effect would, of course, vary from one line to another, thus accounting for the different behavior of the various excitation with the P(33) and the P(38) lines. We have, in this case, the ability to influence the outcome of the reaction by selective excitation with one or another laser line. This is not a result of any mode-specific excitation, however, in fact it just the opposite, since the result is predicted by a statistical (RRKM) model. The effect of changing laser lines is, instead, a more subtle one of varying the amount of energy deposited in the system, which in turn depends on such factors as saturation, frequency matching and pressure broadening. Clearly, any relationship between excitation frequency and reaction product distribution, which it is expected to be evidence for a mode-specific process must be carefully evaluated in terms of energy deposition in the system before such evidence can be accepted.

The predominant role of this elimination in these systems is seen to be a re-elimination mechanism as a precursor for the halaide elimination. This mechanism is characterized by the fact that the halide elimination need not resemble that of the halogenide. Lee and co-workers have observed a re-elimination from CO2-laser-excited CF3-ClCF2 in a molecular beam, and find no energy barrier in the exit channel for this reactant.

The large fraction of re-elimination found in these systems raises the question of whether products characteristic of the possible carbon intermediate could be identified. Allene molecules are known in solution, but only the dihydrogen species has been observed in the gas phase. It is possible, though, that with a parent molecule in which the rearrangement to the olefinic structure is inhibited, the gas-phase carbon could be produced by laser-induced dehydrohalogenation and that its products could be observed.

Stern and co-workers have shown that the mercurophosphate reagent of substituted ethylenes proceed with free rotation about the C=C bond and a-elimination to produce the carbene. Recent observations of inter-system crossing induced by multiple infrared photon absorption, as well as the similarity of the mercuro-phosphate and infrared-multiphoton pathways in this case, suggest that, when the energy content of the molecule is of the order of 100 kcal, the carbene can be vibrationally induced single-triplet mixing may occur. This suggests not only that the vibrational energy is freely distributed among the available modes, but that the electronic excitation and vibrational energy may break down.

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References and Notes

7. Reaction is reported to take place only in the presence of HCl as an added promoter. C2HCl itself does not absorb infrared radiation used to induce the reactions, according to A. R. Burch and A. J. Keen, in Infrared Absorption by \( \text{C}_2\text{HCl, Chem. Phys. Lett.} \) 15, 166 (1977).
10. In the sense that the vibrational excitation of the reacting molecules is not a significantly distributed among vibrational degrees of freedom, or to other molecules present in the system.
11. S. Musallam and J. Ross, J. Chem. Phys. 68, 2155 (1977). and S. Musallam and C. Bechtel, J. Chem. Phys. 89, 2951 (1977) have suggested that energy may indeed excitation in a particular normal mode of vibration as a result of relaxation in a V-V energy transfer. However, modes which are likely to accept vibrational energy is a property of the molecule itself and not of which may have been excited by the infrared pumping process. In addition, the Holstein theory of molecular vibrations, which we employ in the ensuing discussion, assumes that vibrational energy can localize in the reacting part of a molecule. As one of many possible configurations available to a system in which the energy is statistically distributed over all internal degrees of freedom.
Sir: Multiple infrared photon excitation (MIRPE) of \( \text{RC} = \text{CHCl} \) by intense \( \text{CO}_2 \) laser pulses has been found to lead to elimination of HCl. Deuteration labeling studies have shown that the reaction proceeds mainly via a 3-center elimination. This result suggests that vinylidenecarbene \( \text{RC} = \text{C}=\) may be formed during the dehydrohalogenation. Such species are well known in solution, however, the only other gas-phase reaction in which they are formed appears to be mercury-photosensitized 1,1 eliminations. Carbenes, such as \( \text{CF}_2 \), have often been observed in laser-induced multiple-photon dissociation.

In the MIRPE of vinyl chloride \( \text{R} = \text{H}, \text{D} \), acetylene is the sole hydrocarbon product, suggesting that rearrangement of the carbene is extremely rapid, if not concerted with the elimination. This behavior is consistent with expectations that the barrier to the rearrangement \( \text{H}_2\text{C} = \text{C} \rightarrow \text{HC}=\text{CH} \) is extremely low. We have extended our previous work on these systems to substituted vinyl chlorides \( \text{R} = \text{CH}_2, \text{F} \) in order to see whether the rearrangement could be slowed down sufficiently to permit the vinylidenecarbene to exist as a long-lived intermediate.

1-Chloro-2-methylpropene (Aldrich) and 2-chloro-1,1-difluoromethylene (PCR) were used as received except for transfer under reduced pressure to the reaction cell. Infrared spectra prior to MIRPE showed no major impurities to be present. The compounds were photolyzed with the 9.6-\( \mu \text{m} \), \( \text{P}(16) \) or \( \text{P}(18) \) and 10.6-\( \mu \text{m} \), \( \text{R}(18) \) \( \text{CO}_2 \) laser lines, respectively, either alone at pressures of 4-5 torr or in the presence of added gases. The gaseous product mixtures were collected and analyzed by GC/MS (H-P 5890 A or Hitachi RMU-61).

The MIRPE of \( \text{CH}_2\text{CL} = \text{CHCl} \) leads to HCl (observed in the product infrared spectrum) and butadiene as major products, with smaller amounts of allene, 2-butyne, and diacetylene. Photolysis in the presence of \( \text{CH}_2\text{O}, \text{H}_2\text{O}, \text{NH}_3, \text{H}_2\text{S}, \text{or D}_2\text{S} \) vapor yielded no additional products. These results suggest that the \( \text{CH}_2\text{CL} = \text{C} \) formed by loss of HCl rearranges extremely rapidly, either by methyl migration across the double bond (eq 2) or by intramolecular insertion (eq 3). Since the acetylenic form is \( \sim 30-40 \text{ kcal/mol} \) more stable than the carbene, the resulting 2-butyne, if formed, would contain a large amount of excess vibrational energy. Some of this could be stabilized by collisional relaxation.

**Formation of Vinylidenecarbene Intermediates in Multiple Infrared Photon Elimination Reactions**

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but the principal route seems to be further rearrangement to the split more stable isobutylene. The same products could be derived from the methylene intermediate since the ring can open to form the butene directly at the butadiene by way of the ketene. A possible test of this proposed mechanism would be to deactivate selectively these intermediates and quench further rearrangement by adding an inert buffer gas. It must be remembered, however, that increased collisions can also influence the MIRPE process itself and thus the mean excitation in the products.

It may be noted that ethyne is also found when CF,Cl, is photolyzed in the presence of (CH),C=CH, and results from secondary redistribution exist in CH,CH,=C=CH, Diacetylene appears to be a ubiquitous side product in reactions of this type.

The behavior of CF,C=CHO under the same conditions is quite different. Aside from HCl, the principal products are CF, (167%) and CF,H (35%). No CF, is observed. In the presence of added H,SO at CH,OH, the products are CF,Cl, (183%), CF,H (12%), and CF, (1%). It seems clear that, in this system, the CF,C=CHO species is long-lived, with essentially no rearrangement taking place to the acetylene. In the presence of labile hydrogen, the dominant reaction path seems to be H abstraction to form stable dehalos. A possible mechanism to form the CFs would be secondary MIRPE of the unsaturated intermediate to form CF, plus free carbon. A small amount of C=C formation in the pure CF,C=CHO is consistent with this possibility. When the photolysis is carried out in the presence of D, the principal product is CF,OD, with a lesser amount of CF, D and small amounts of the previously mentioned products. The presence of CF,OD confirms the existence of CF,C=CHO, the large amount of CF,OD suggests that a C-Cl homolysis channel, to form CF,O, is also important in this system. The chemistry of this system is, indeed, quite complex, since several dissociation channels following MIRPE are available.

These results demonstrate that, not surprisingly, dihalovinylidene does not undergo rearrangement and can readily be trapped by hydrogen donors, whereas isobutenylene undergoes rearrangement more rapidly than it can be trapped. Since (CH),C=CHO, can be trapped in solution, the activation barrier to rearrangement must be no less than 10-15 kcal/mol or so. In the case of HF=CF,C, Schaefer and co-workers have predicted a large barrier to rearrangement: 1.85 kcal/mol. For the rearrangement

$$F_2C=CO \rightarrow F_2C=CP$$

however, a semiquantitative MO calculation predicts an activation barrier -50-60 kcal/mol higher than that for reaction 1. The greater vibrational complexity of CH,C=CH, as compared with CH,C=CH, will lead to a partitioning of absorbed infrared energy into internal modes of the first named species, thus providing sufficient energy to surmount the barrier. For the parent or dibromo, the lower degree of vibrational excitation is sufficient to permit reaction 1 to occur, but not reaction 4, with its appreciably higher barrier.

This work illustrates how the MIRPE process may be used in chemical investigations by permitting the preparation of primary dissociation products or unstable intermediates at a high instantaneous concentration in the presence of cold diluent. Spectroscopic characterization of species such as vinylidenecarbenes, which have hitherto not been directly observed, may be possible in this way.

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References and Notes

(3) Analogous results have been obtained in fluorinated ethylenes by C. N. Ock and J. Wrig, J. Chem. Phys. 89, 1201 (1978).
(11) The GC-MS analysis did not permit us to distinguish between the two possible isomers, CH=CH=CH and CH=CH=CH.
(15) Using an impulsive-homocollision model and the data on rotational energy release following MIRPE of CH,C=CHO, we estimate an activation energy of 15-20 kcal/mol in the CH,C=CHO system but only 2-3 kcal/mol for H,C=CHO or F,C=CHO. To the extent that one can trust such a rough estimate, this result suggests that the barrier calculated for rearrangement is not too high.

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Appendix C. Synthesis of C₂H₂DCl

Two isomers of d₁-vinyl chloride were prepared, trans-d₁-vinyl chloride [C.1] and α-d₁-vinyl chloride [C.2].

C.1 trans-d₁-vinyl chloride

\[
\text{C}_2\text{H}_2 + \text{HgCl}_2 \xrightarrow{6\text{N HCl}} \text{ClHgC} = \text{C} - \text{C} \xrightarrow{\text{NH}_3} \text{HgC} = \text{C} - \text{Cl}_2
\]

A 6N HCl solution was prepared by adding 60 ml conc. HCl to 40 ml boiled distilled water in a 250 ml flask. 96 g HgCl₂ were added and dissolved with ease. Welding grade acetylene was bubbled into the solution with a sintered glass bubbler; the excess gas was bubbled through water to prevent backstreaming of air. After 2 hours a white soapy precipitate began to form.

The precipitate was filtered off every 20 min or so to avoid clogging the bubbler, and continued to form for several hours. It was difficult to dry even in a vacuum desiccator. The precipitate can be recrystallized to fluffy white needles from benzene and showed an NMR doublet at δ 6.28, δ 6.34, affirming its identity as trans-chlorovinyl mercury chloride (I) [C.3].
Attempts at synthesizing trans-dichlorovinyl mercury (II) from I failed. A 40 ml sample of benzene saturated with I was placed in a dropping funnel. Upon addition of 40 ml ammonia a sticky dense white precipitate formed. The precipitate was difficult to collect and dissolved when washed with water. The remainder dried to a hard white solid which resisted attempts at dissolution.

DBr was synthesized by adding fresh D2O dropwise to fresh boiling PBr3. The gas was collected through a water condenser and an ice-cooled trap into a LN2 cooled flask. Its IR spectrum showed at least 95% isotopic purity. The DBr was admitted to a 250 ml Erlenmeyer flask containing 25 ml of dioxane; the flask was shaken for one hour. The dioxane was then added to 26 g of I in a 3-necked RB flask sitting in a 50°C oil bath. Gas was collected by slowly flowing dry N2 over the dioxane with continuous stirring. The N2 stream passed through an ice cooled trap and two LN2 traps. After one hour the contents of the two LN2 traps were collected through a KOH/CaCl2 filled tube into a gas flask. Its IR spectrum compared favorably with that published [C.3] for trans-δ1-vinyl chloride, showing about 96% isotopic purity with traces of moisture and acetylene. The ratio of trans to cis isomers was about 9:1.

Acetylene was cleaned from the mixture with a simple procedure. A solution of 10 ml water and 5 ml conc. nitric acid was saturated with silver nitrate. This solution was
frozen in a small flask with a ground glass neck. The gas mixture was then frozen into the flask. The contents were allowed to thaw, then were shaken for 30 minutes, during which a small amount of a white precipitate (presumably silver acetylide) formed. The gas in the flask was then frozen into a second flask containing loose P₂O₅ as a drying agent. Finally, the gas was frozen into a storage bulb. Its spectrum showed no trace of acetylene or moisture.

C.2 α-δ₁-vinyl chloride

\[
\begin{align*}
C₂HCl₃ \xrightarrow{\text{CaO}} & \quad \text{CaO} \quad \xrightarrow{\text{H₂O}} \quad \text{CH₂CCl₂} \xrightarrow{\text{DBr}} \quad \text{CH₂BrCDCl₂} \\
\text{III} & \quad \text{UV} \quad \text{(cold)} \quad \text{IV}
\end{align*}
\]

I,1-dichloroethene (vinylidene chloride, III) was prepared from 1,1,2-trichloroethane by refluxing 30 ml in 120 ml water and 18 g CaO for 4 hours. The alkene was distilled off at 1 atm (bp = 32°) and redistilled using a Vigreux column. The yield was 17 ml or 66%; the product was identified by IR and NMR and stored over hydroquinone to prevent polymerization. III is also commercially available.

DBr was synthesized as described in the preceding section.

1,1-dichloro-2-bromoethane-1-d₁ (IV) was synthesized in a quartz flask fitted with a dry ice and acetone cooling collar.
15 mls of III were distilled into the flask in vacuo, followed by 20 ml of DBr, using LN$_2$ cooling. The contents melted upon removal of the LN$_2$ and refluxed from the dry ice/acetone cooled portion of the flask. A UV photoreactor (courtesy of the undergraduate laboratory) utilizing 15 Hg lamps was then employed to irradiate the reactants for 2 hours. The coolant was removed from the collar and excess reactant pumped off. The product (IV) was washed from the quartz flask with methylene chloride, treated with a saturated solution of sodium bicarbonate, dried over CaCl$_2$ and distilled (bp = 90$^\circ$ at 140 Torr). NMR revealed a broad peak at 64.2. Recovery was 12 mls, or about 46% yield.

Six ml of IV was added over a 50 min. period to a refluxing suspension of Zn dust in 40 ml of ethanol. The evolved gas passed through two ice traps and was collected in a LN$_2$ cooled trap. The gas was passed four times over dry CaCl$_2$ in bulb to bulb distillations, after which no trace of EtOH was seen in the IR spectrum. The spectrum agreed well with that of [C.4] with excellent isotopic purity. About 2.6 g were recovered.
APPENDIX D. "Energy deposition in molecules resulting from multiple infrared photon absorption"


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Energy deposition in molecules resulting from multiple infrared photon absorption

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Abstract. The most important factor determining the response of systems to high-intensity infrared radiation is the quantity of vibrational energy deposited in the absorbing molecules. Determination of this quantity is complicated by spatial nonuniformities in the infrared radiation fluence and by distributions over energy in the system. In this paper, we obtain expressions for the infrared fluence distribution in a focused Gaussian beam. This is combined with an empirical model for the excitation function to calculate energy deposition for a range of parameters. These results are compared with available experimental data on dissociation yields for sulfur hexafluoride, and also to various approximate results. Finally, we consider the advantages and limitations of several possible experimental approaches to determining the absolute excitation level of molecules and microscopic energy distributions in the focal volume of the laser beam.

Key Words: laser/chemistry, multiple phoan effects, molecular decomposition, Gaussian beams.

INTRODUCTION

In any experiment which measures the overall response of a system caused by irradiation of a sample, such as energy deposition, absorption cross section at the radiation wavelength, or net dissociation yield, determination of the intensity distribution of the radiation is of fundamental importance. Physical theories which explain the effect must account for the intensity dependence of its magnitude or extent. In principle, parameters characteristic of the radiation field, such as intensity or fluence (integrated intensity), should be precisely determinable with the use of an appropriately calibrated transducer. However, variations in intensity throughout the sample may make it difficult to relate a measured effect to a particular value of the intensity. While the necessary procedures may be relatively straightforward for well-collimated beams, it is often necessary to employ strongly focused beams, especially for the dissociation of small molecules. Thus, some procedures must be used to link the measured effect, the overall beam intensity, and the focusing optics used in the experiment. In this paper, we will consider the technique for dealing with beams of Gaussian cross section appropriate for laser applications, such as the problem of multiple infrared photon absorption in gases.

Several authors have used various approximations to model their particular optical geometries. In most multiple photon experiments, the exact beam cross-section function is not known, especially if the experiments utilize a focused beam. It is therefore difficult to separate those effects which are caused by the wide range of intensities intercepted by the sample from those which are caused by the fundamental microscopic dynamics. The data must be corrected for the geometrical form of the beam before the empirical results can be compared with a physical model. Since the geometry of Gaussian beams is well characterized, the extraction of purely dynamical effects becomes fortuitously analytic, as has been demonstrated.14 We wish to present a consistent approach here, to consider the implications of the beam geometry for various types of Gaussian beams, and to illustrate the shortcomings of "deconvoluted" data.

DEFINITIONS

Whenever possible, we will adhere to the notation found in Yariv,1 including the following definitions:

\[ I(r,z) \] - location of focal plane on propagation (z) axis
\[ w_0 \] - spot size at focal point: radius to 1/e^2 point of field
\[ r(z) \] - spot size at axial point z
\[ R(z) \] - radius of curvature at z
\[ \zeta(z) \] - axial distance at z
\[ \Phi \] - energy fluence; for pulsed beams, \( \Phi = \int (\text{intensity}) \, dt \)
\[ V(\Phi) \] - volume in beam experiencing fluence \( \Phi \) or greater
\[ \eta(\Phi) \] - change in \( V(\Phi) \) per unit fluence
\[ \sigma \] - molecular density
\[ \lambda \] - wavelength of radiation

PROPERTIES OF THE BEAM

We will consider "TEM_00" Gaussian beams, for which the intensity I follows:

\[ I(r,z) = E_0^2 E^2 = I_0 \frac{w_0^2}{w^2(z)} \exp\left(-\frac{2r^2}{w^2(z)}\right) \]  

where

\[ w(z) = \sigma \left[ 1 + \left( \frac{r}{\zeta(z)} \right)^2 \right]^{1/4} \]  

The fluence \( \Phi(r,z) \), which is of great importance in multiple
ENERGY DEPOSITION IN MOLECULES RESULTING FROM MULTIPLE INFRARED PHOTON ABSORPTION

Photon chemistry, \( \psi_{\text{ch}} \), has the same form as the intensity, Eq. (1), therefore describes \( \psi_{\text{ch}} \) as well. Subscripts \( z \) and \( \lambda \) will be used to denote orthogonal transverse directions. To avoid confusion, we will define circular beams at time for which \( \omega_{z} = \omega_{\lambda} = \omega_{\lambda 0} \), occurring at \( z(0) \), elliptic beams whose for which \( \omega_{z} = \omega_{\lambda} = \omega_{\lambda 0} \), constant \( \omega_{z} \), occurring at \( z \neq 0 \), and finally elliptic confocal beams at those having \( \omega_{z} = \omega_{\lambda} = \omega_{\lambda 0} \). The generic term elliptic refers to elliptic or elliptic confocal beams.

One can characterize the light beam by specifying the complex beam radius \( q(z) \) at some point \( z \),

\[
\frac{1}{q(z)} = \frac{1}{R(z)} - \frac{1}{\omega_{\lambda 0}^2(z)}
\]

where

\[
R(z) = z(1 + \frac{\omega_{\lambda}^2}{z^2}).
\]

For our purposes it will be of greater use to know the spot size \( \omega_{0} \) and its location \( z(0) \), such as the waist inside a stable resonator, through distances and optics. A combined ray transfer matrix elements are \( \text{abcd} \), and finally a distance \( z \) to \( z(0) \). The total ray transfer matrix \( M \) for propagation from \( z = 0 \) to \( z(0) \) is

\[
M = \begin{bmatrix} 1 & I \\ 0 & 1 \end{bmatrix} \begin{bmatrix} a & b \\ c & d \end{bmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix}
\]

Using the ABCD law of Gaussian beam propagation, \( q(z(0)) \) from \( q(z(0)) \) and matrix \( M \):

\[
q(z(0)) = Aq(z(0)) + B
\]

At \( z(0) \), \( R(z(0)) = 0 \). Combining Eqs. (4) and (6), we can express \( \omega_{0} \) as

\[
\omega_{0} = \frac{\omega_{0 0}}{\sqrt{I}}
\]

The distance \( I \) at which the spot size reaches \( \omega_{0} \) can also be found from the condition that \( R(z(0)) = 0 \); straightforwardly one obtains

\[
I = -(d_b + c\omega_{0})/(c_\lambda^2 + d_\lambda^2).
\]

Thus, by knowing the location and size of a beam waist, and all optics from that point to the region of interest, one can easily compute the location and size of the second waist.

In practice, however, a pure \( \text{TEM}_{00} \) mode may be difficult to obtain from a pulsed laser and some spatial filtering may be necessary to exclude unwanted beam components. For such systems the location and size of the beam waist can be determined empirically, using simple measurements and tools, such as a scanning photodiode or variable aperture. Since the beam is most intense at \( z(0) \) and may cause plasma at obstructing surfaces, direct measurement of the beam waist may be difficult. Sufficiently far from \( z(0) \), however, the beam expands asymptotically to the cone whose half apex angle is

\[
\theta = \tan^{-1} \left( \frac{\omega_{0}}{\omega_{\lambda 0}} \right).
\]

If the spot size of the beam is measured at two points \( z_1 \) and \( z_2 \), we have

\[
\tan \theta = \frac{\omega(z_1) - \omega(z_2)}{z_2 - z_1}
\]

Equation (10) combined with Eq. (6) yields

\[
\omega_0 = \frac{1}{\omega_{\lambda}(0)} \frac{z_2 - z_1}{z_2 - z_1}
\]

Since the apex of the cone defines \( z(0) \), we find \( z(0) \) simply:

\[
z(0) = z_2 - \omega(z_1) \cos \theta = z_2 - \omega(z_1) \cos \theta.
\]

Thus from two measurements of the beam cross section one can easily find the location and size of the beam focus.

Equations (4)-(12) are valid for circular as well as elliptical beams, and allow the relative magnitude of the fluence to be specified in the region of interest. The absolute magnitude of the fluence can be found using a joulmeter, which measures the total pulse energy.

\[
E_T = \int_0^\infty \Phi(z,2\pi dr)
\]

where it is assumed that the dimension of the joulmeter face is much larger than \( \omega(z) \). For convenience, we evaluate Eq. (13) at \( z = z(0) \), so that for circular beams

\[
E_T = \int_0^\infty \Phi(z,2\pi dr) = \int_0^\infty \frac{\omega_{0 0}^2}{2}
\]

For elliptical beams, Cartesian coordinates are suitable variables of integration:

\[
E_T = 4 \int_0^\infty \Phi(x,y,z(0)) dxdy = \int_0^\infty \frac{\omega_{0 0}^2}{2}
\]

The correspondence in Eqs. (14a), (14b) between \( E_T \) and total power, and between \( \Phi_{\text{0}} \) and peak intensity, can be seen easily.

DETERMINATION OF CRITICAL VOLUMES

Of critical interest in our analysis is the number of particles intercepted by the beam. If the particle density \( \Phi \) is given, a suitable volume inside the beam can be found which contains the particles under study. Many authors have derived expressions for volumes pertinent to their respective applications; Keeler et al. obtained an expression for the volume enclosed by an isointensity (iso-fluence) surface in a Gaussian beam.

\[
V(\Phi) = \frac{\Phi_{\text{0}}^2}{\Phi} \int_0^U (1 + U)^4 \ln(K(1 + U))dU
\]

where

\[
K = \Phi_{\text{0}} \Phi
\]

\[
U = \left( \frac{1}{K} \right)^{1/5}
\]

\[
U = \frac{\pi z(0)}{\omega_{\lambda 0}}
\]

Eq. (15) can be evaluated exactly, yielding

\[
V(\Phi) = \frac{4}{3} \Phi_{\text{0}}^3 \left( U - \cos U \right) \frac{1}{2}
\]

where \( U = U’ \). Equation (16) reduces to Keeler’s result when all terms are dropped but the last, proportional to \( U’ \). A similar expression can be obtained for the corresponding volume in an elliptic beam.

\[
V(\Phi) = \frac{4}{3} \Phi_{\text{0}}^2 \left( U - \cos U \right) \frac{1}{2}
\]

where each integral extends between zero and the appropriate upper bound.

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After two integrations of Eq. (17), we obtain
\[ V(\phi) = m \omega_0^2 \omega_{po} \int_0^z \ln \left( \frac{m \omega_0}{K w_0(z)} \right) \, dz \]
\[ = \frac{m}{\lambda} \omega_0^2 \omega_{po} (m - \tan^{-1} m) \]
where \( m \) is analogous to \( U \) in the circular beam case.
\[ m = \left( \frac{1}{K} \right)^{1/2}. \]

For the elliptic conical case, evaluation of Eq. (17) is more difficult. The upper bounds are given by
\[ x' = \left[ \frac{w_0^2}{8} \left( 1 + \frac{w_0^2 \omega_{po}^2}{K w_0(z)} \right) - \frac{2y^4}{K w_0(z)} \right]^{1/2} \]
\[ y' = \left[ \frac{w_0^2}{2} \ln \left( \frac{w_0^2 \omega_{po}^2}{K w_0(z)} \right) \right]^{1/2} \]
\[ z' = \frac{2}{k} \left( \frac{1}{m} - \frac{1}{k} \right)^{1/2} \]
After two integrations, we obtain
\[ V(\phi) = \frac{m}{\lambda} \omega_0^2 \omega_{po} \int_0^z \ln \left( \frac{m \omega_0}{K w_0(z)} \right) \, dz \]
which must be evaluated numerically. Values of \( V(\phi) \) for a range of \( K \) and \((w_0 / \omega_{po})\) are given in an Appendix.

For values of \( \phi \) small with respect to \( \phi_0, K < 1 \). In this limit, \( V(\phi) \to \phi \) for circular beams. From Eq. (15), \( V(\phi) = \phi \), for elliptic beams. Figure 1 shows the dependence of \( V(\phi) \) on \( \Phi \), where the quantity \( V \) plotted is the dimensionless quantity in parentheses in Eq. (16) or (20). The differential volume, or change in volume per unit change in \( \Phi \),
\[ \frac{dV(\phi)}{d\phi} \]
\[ = \frac{\phi}{\phi_0} \frac{\omega_0 \omega_{po}}{K} \left[ \frac{1}{2} - \frac{\phi}{\phi_0} \right] \]
\[ \frac{\phi}{\phi_0} \frac{\omega_0 \omega_{po}}{K} \left[ \frac{1}{2} - \frac{\phi}{\phi_0} \right] \]

where the quantity \( \omega_0 \) is the threshold fluence \( \phi_0 \) for dissociation in multiple photon chemistry experiments. It would be valuable, therefore, to know at what \( \phi_0 \) it is that \( V(\phi_0) \) maximizes, or for what \( \omega_0 \)
\[ \frac{dV(\phi_0)}{d\omega_0} = 0. \]

Straightforwardly differentiating Eq. (13) with respect to \( \omega_0 \), one obtains
\[ \frac{dV(\phi)}{d\omega_0} = \frac{2 \omega_0^4}{\lambda} \left( 15 \phi_0 - 24 \tan^{-1} \phi_0 \right) \]
which vanishes at \( \phi_0 = 3.234106 \ldots \), implying \( \phi = 2.751403 \phi_0 \). Thus, for given parameters \( E_T \) and \( \phi_0, V(\phi_0) \) maximizes when
\[ \omega_0 = \left( \frac{E_T}{2.751403 \phi_0} \right)^{1/2} = 0.481 \left( \frac{E_T}{\phi_0} \right)^{1/2}. \]

For elliptic beams, we have
\[ \frac{dV(\phi)}{d\omega_{po}} = \frac{2 \omega_0^2 \omega_{po}^2}{\lambda} \left[ 2m - 3 \tan^{-1} m \right] \]
which vanishes at $m = 1.451104$, implying $E_T' = 1.782\, E_T$, and thus for $E_T$, $\Phi_R$, and $w_{0y}$:

$$\Phi_R = \frac{E_T}{2.785\, w_{0y}}$$

(30)

$V(\Phi_R)$ increases monotonically with decreasing $w_{0y}$ in this case. Also, it can be shown that there is no elliptical configuration which renders a larger $V(\Phi_R)$ than the circular case when Eq. (29) holds, with constant $E_T$ and $\Phi_R$.

**TREATMENT OF EXPERIMENTAL DATA**

In an experiment in which a net quantity is measured from the irradiation of a sample with a Gaussian beam, various portions of the sample experience vastly different fluence intensities: The net quantity is thus the sum of the response of the system over all portions of the beam used. Interesting physical theories, however, describe a system’s response at a particular value of the fluence, and not over the whole beam simultaneously. Therefore, it would be of value to extract the system’s response at particular fluences from experimental data (deconvolution) and to describe an experimental result using a physical theory (convolution). For elliptical Gaussian beams, Kolden et al. have already deconvoluted the technique of deconvolution. Briefly, the total response $C_T$ per unit length of beam used is expressed as the weighted average of the system’s response function $g(\Phi)$ over the beam area:

$$C_T = \int_0^{E_T} g(\Phi)\, d\Phi$$

(31a)

$$= \int_0^{E_T} g(\Phi)\, \frac{w_{0y}}{E_T}\, dv$$

(31b)

Taking the derivative of Eq. (31) with respect to $\Phi$ at $\Phi_0$ and recalling Eq. (4a), we have:

$$g(\Phi_0) = \frac{dC_T}{d\Phi}$$

(32)

Equation (34) holds for circular beams as well as elliptical unfocused beams.

For other beam shapes, however, the change of variables between Eq. (31a) and (31b) cannot be made, but the general scheme can still be applied. For a general beam type we use as a starting point:

$$E_T = \int_0^{E_T} g(\Phi)\, v(\Phi)\, d\Phi$$

(33)

where $E_T$ is the total response. Taking the derivative of Eq. (33) with respect to $\Phi$ and evaluating at some fluence $\Phi_0$, we obtain:

$$g(\Phi_0) = \frac{dE_T}{g(\Phi_0)\, v(\Phi_0)\, d\Phi}$$

(34)

which is a general deconvolution equation. For focused beams, $v(\Phi)$ diverges so that a convenient $\Phi$, must be chosen, such as $\Phi = w_{0y}$, $k < 1$.

For focused circular and elliptical beams respectively, Eq. (34) becomes:

$$g(\Phi) = \frac{1}{\Phi(\Phi_0)}\, \frac{w_{0y}}{2k}$$

(36a)

In Eqs. (36) the derivatives are merely the local slopes of the $E_T$ vs. $E_T'$ graph. Taking small differences between large numbers of finite precision produces a noisy derivative, smoothing may be necessary.

Convolution of the empirically or theoretically derived function $g(\Phi)$ can be accomplished by numerical evaluation of an integral equation such as Eq. (70). As an example, let $g(\Phi)$ be the absorption cross-section function. The energy absorbed $E_D$ in a cell of length $2t$ and radius $r$ much greater than the beam radius, centered at $z(0)$, could be modeled as:

$$E_D = w_{0y} \int_{z(0)}^{z(0)+t} \int_{-t}^{t} g(\Phi)(\Phi, \Phi, \Phi)\, dv\, dr$$

(37)

The value of such a convolution lies in the freedom to choose the limits of integration to conform to the physical volume of interest in the experimental apparatus. A serious shortcoming of the technique lies in the nature of its formulation and in the experimental method. When a value for $g(\Phi)$ is found, it must be the average response function for all molecules experiencing fluence $\Phi$. It is therefore a first moment of the microscopic distribution of molecules over response, and may not lead directly to descriptions of other responses which are sensitive to the shape or temporal behavior of the microscopic distribution.

Taking energy deposition again as an example, the response function $g(\Phi)$ is actually the average cross-section for absorption over whatever distribution of molecules over absorbed energy $P(E;\Phi)$ is formed when an ensemble of molecules is subjected to fluence $\Phi$:

$$g(\Phi) = \frac{\int_{E_T}^{E_T} \int_{E_T}^{E_T} P(E;\Phi)\, dE}{\int_{E_T}^{E_T} \int_{E_T}^{E_T} P(E;\Phi)\, dE}$$

(38a)

$$= \frac{\int_{E_T}^{E_T} \int_{E_T}^{E_T} P(E;\Phi)\, dE}{\int_{E_T}^{E_T} \int_{E_T}^{E_T} P(E;\Phi)\, dE}$$

(38b)

The distribution function $P(E;\Phi)$ reflects the dynamical physics of the absorption process, but is not determined by measurements which detect only averages over $P(E;\Phi)$, such as absorption.

Example: multiple photon absorption

To highlight such difficulties, and to illustrate the effects of the range of fluences in a focused circular Gaussian beam, we consider the problem of multiple infrared photon absorption and consequent dissociation of SFs. Although much data has been published for this molecule, the data taken using beams of well-characterized Gaussian cross section are scarce. Dissociation experiments typically utilize TEA lasers operating in a multimode or unstable resonator configuration; the actual fluences at all points in these beams are not known exactly. The convolution of a dissociation cross-section function with some model of the fluence distribution becomes at best only approximate.

For energy absorption, many careful measurements have been made. The data of Ambartsumian et al. and of Black et al. extend to $\sim 10$ J/cm$^2$ and are depicted in Figure 2 along with an arbitrary fit used for ease in computation. For Ref. 22, the fit used was:

$$<a(\Phi) > = 9.333 \times \frac{1}{0.06 < < 1.3}{10.475 \times \frac{0.161}{1} + 0.23}{1.5 < \Phi < 1.5} \times \frac{1}{0.06 < < 1.3}$$

(39)

and for Ref. 23:

$$<a(\Phi) > = 9.15 \times \frac{1}{0.06 < < 2.35}$$

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distribution a \& r 5 option if 
where $P(EK>E)$ is the particular form of 
we wish to 
us equilibrium distribution may also depend on 
model multiple photon absorption fairly 
was made to the 
desorved data of Ref. 23 in Ref. 22, only a rough estimate of 
the fluence was made for fluences between 1 and $10 \text{ J/cm}^2$. Using 
these data, an estimate of the total energy absorbed in a beam of 
arbitrary shape can be computed.

To model dissociation of SF$_6$ molecules, however, more 
dynamical information must be obtained. The shape of the 
distribution of molecules over absorbed energy at a particular 
average absorbance $P(E,\langle E\rangle)$ must be specified. This shape of 
$P(E,\langle E\rangle)$ has not been determined, but may be narrower\textsuperscript{14} or 
broad\textsuperscript{er\textsuperscript{14} than a thermal distribution at the same $\langle E\rangle$. There is 
some evidence\textsuperscript{14,15} that a Boltzmann-like distribution itself 
can model multiple photon absorption fairly well. The shape of the 
nonequilibrium distribution may also depend on $\langle E\rangle$.\textsuperscript{16} For instance, being proportionately broader at high $\langle E\rangle$ 
than at low $\langle E\rangle$. For lack of dynamical information, however, and because 
we wish to avoid the dynamical details of the multiple photon 
absorption process, we will assume that the distribution is 
Boltzmann-like,

$$P(E,\langle E\rangle) = \frac{N(E)\exp(-\gamma\langle E\rangle)}{\int_{0}^{\infty} N(E)\exp(-\gamma\langle E\rangle))dE}$$  

(43)

where $P(E,\langle E\rangle)$ is the particular form of $P(E,\langle E\rangle)$
corresponding to the maximal entropy assumption.\textsuperscript{14} In Eq. (42), $N(E)$ is 
the density of vibrational states per unit energy at vibrational 
energy $E$, and $\gamma\langle E\rangle$ is a parameter analogous to $(kT)^{-1}$. \textsuperscript{14} Details of 
the computation of the Whitten-Rabinovitch function\textsuperscript{14} for 
$N(E)$ and of the RRKM rates\textsuperscript{14} used below can be found in Ref. 23. 
A description of $\langle P(E)\rangle$ is in Ref. 32.

Computationally, the influence of $P(E,\langle E\rangle)$ on the total 
distribution $P(E)$ of all molecules in the beam can be easily seen. 
When $P(E,\langle E\rangle)$ is summed over all values of $\langle E\rangle$ resulting from 
the Gaussian dependence of the fluence, the spatially averaged 
distribution $P(E)$ can be expressed as

$$P(E) = \frac{1}{\Phi_m} P(E,\langle E\rangle)\langle E\rangle d\langle E\rangle$$  

(43)

where $\Phi_m$ is a convenient lower bound, which is $0.5 \text{ J/cm}^2$ in these 
computations, and $\langle E\rangle$ is given as a function of $\Phi$ by Eq. (39) or 
(40). Figure 3 shows $P(E,\langle E\rangle)$ as a delta function at $E = \langle E\rangle$ and when it is expressed by Eq. (42). Over a large range of 
vibrational energies, the two curves are determined largely by the 
beam shape. At high energies, the thermal "tails" of distribution 
$P(E,\langle E\rangle)$ are manifest as that part of $P(E)$ extending beyond $E = \langle E\rangle$.\textsuperscript{14}

Decreasing the spot size of the beam increases the peak fluence 
and hence the number of molecules reaching very high energies. 
Using Eq. (38) as a model of absorption (even though the ex.
ENERGY DEPOSITION IN MOLECULES RESULTING FROM MULTIPLE INFRARED PHOTON ABSORPTION

Turning points do not extend beyond $\sim 10^4$ cm$^{-1}$ and disregarding dissociation, we show in Figure 6 the effect on $\nu(E)$ of decreasing $\omega_0$ while keeping $\nu_T$ and $\Phi_0$ constant. Even though the average number of photons absorbed per molecule does not change greatly the fraction extending beyond $\sim 10^4$ kcal mole increases dramatically with $\Phi_0$. For comparison, curve (c) is $P(E)\langle E \rangle_t$ for $\langle E \rangle_t = 35.2$ kcal mole, the average energy in distribution (d).

In the absence of a detailed dynamical model which describes simultaneous absorption and dissociation, using distributions such as those in Figure 6 to model dissociation is a crude approximation to the actual dynamical process. If two conditions are met, however, the model becomes more tenable. These are that (i) the pumping be much faster than the $V = T$ relaxation rate and that (ii) at fluences near the threshold $\Phi(t)$ for reaction $\Phi_E$ (see below) the values of $<n>(\nu_0)$ be well known. Condition (i) is met using $\nu_{\text{pump}} = 10^3$ sec$^{-1}$ and $\nu_{\text{relax}} = 10^2$ sec$^{-1}$ which are reasonable parameters. Condition (ii) specifies that for those values of $<E>$ where significant portions of the microscopic distribution $P(E,<E>)$ contribute to dissociation, the function $<n>(\nu_0,E) = <E>$ should be accurate. For sufficiently high fluences, $<E>$ approaches and exceeds the activation energy of the reaction $\Phi_E$ and the exact magnitude of $<E>$ need not be known as accurately.

We will use a method similar to that of Black et al. for computing the fraction of molecules $P(E)$ dissociated at internal energy $E$.

$$P(E) = \frac{k_{\text{REM}}(E)}{k_{\text{REM}}(E) + k_{\text{RELAX}}(E)}$$

(44)

In Eq. (44), $k_{\text{RELAX}}$ will be held constant at $10^5$ sec$^{-1}$ and $k_{\text{REM}}(E)$, the REM microsopic rate at energy $E$, is computed exactly as Ref. 22. The total number of molecules dissociated divided by the molecular density yields the equivalent volume $V_B$ of particles dissociated.

$$V_B = \frac{1}{E_T} \int_0^\infty P(E) \langle E \rangle_t dE$$

(45a)

where the integral over $E$ need not be evaluated below $E_T$, where $P(E)$ is zero, or above a convenient $E^*$, where $P(E)\langle E \rangle_t$ becomes very small. The order of integration can be reversed in Eq. (45b).

$$V_B = \frac{1}{E_T} \int_0^\infty P(E) \langle E \rangle_t dE$$

(45b)

so that the integrals over $E$ need to be evaluated only once for each $\langle E \rangle_t$. The volume $V_B$ is analogous to the reaction volume of Keefe et al.4.

Figure 5(b) shows the dependence of $V_B$ on $\omega_0$ as computed from Eq. (45b), for both functions of $\omega_0=10,1/10$, i.e., Eqs. (30) and (41). The resemblance to Figure 5(a) is undeniable, indicating that the dissociation follows the geometry of the beam even when the dispersion $P(E)\langle E \rangle_t$ is included. In other words, the net dissociation is determined largely in the region of $E$ where the two curves of Figure 5 are very close. Moreover, the curves in Figure 5(b) maximize at the $\omega_0$ predicted by Eq. (29) (indicated by an arrow) when $\Phi_0$ is taken from Figure 5 (see below). This indicates that the frequency threshold model of Keefe et al.4 may be a valid description of the system for values of $E$ larger than originally supposed.

Figure 6. (a) Reduced volumes $V_\text{R}(\nu_0)$ for $\Phi = 1.1$ J cm$^{-2}$, $\nu_T = 0.1$, $I = 10^{-7}$ W cm$^{-2}$, for (1) circular beam, $V_\text{R} = 2.1$, (2) beam $U = 10^6$ and (2) adiabatic beam. $V_\text{R} = 2.1$ J cm$^{-2}$ (2). (b) Reduced volumes $V_\text{R}$ of dissociated $S\Phi$, as a function of $\omega_0$ in a circular beam for $\Phi_0=10^4$ given by (1) Eq. (38) and (2) Eq. (140), and $k_{\text{RELAX}} = 10^5$ sec$^{-1}$.

Using Eq. (18) one may find the fluence $\Phi_R$ for which $V_\text{R} = V_\Phi(\Phi_0)$. These are plotted in Figure 6. At large $\omega_0$, $V_\text{R} \rightarrow 0$ at $\Phi_R = \Phi_0$. At smaller $\omega_0$, however, a fluence threshold is reached, which depends greatly on the model of $\langle n_0\rangle(\Phi)$ and weakly on $k_{\text{RELAX}}$. Using Eq. (38), the threshold is attained at $\Phi_R = 11$ J cm$^{-2}$, where the data become less accurate. The data of Black et al.4 are less uncertain in the region of $\Phi_R = 6$ J cm$^{-2}$, but agreement with the empirically determined $\Phi_R = 11$ J cm$^{-2}$ is not achieved.

The failure of these calculations to replicate the fluence threshold can be attributed to several sources. The main weakness in the model lies in condition (ii), that is, in the region of fluence of the assumed $\Phi_R$ and somewhat higher, the calculation of $\Phi_R$ is very sensitive to $\langle n_0\rangle(\Phi)$ for $\omega_0$ up to $\sim 30 = \omega_0$ by. Furthermore, the original data for $\langle n_0\rangle(\Phi)$ have a finite uncertainty within which the extrapolated function $\langle n_0\rangle(\Phi)$ and hence $\Phi_R$ may fluctuate considerably. Also, the form of the distribution $P(E)\langle E \rangle_t$ may actually be broader than the Boltzmann-like...
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APPENDIX E. "Infrared double resonance of SF$_6$ with a tunable diode laser"


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Infrared double resonance of SF₆ with a tunable diode laser


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Double resonance spectroscopy has been carried out on the ν₁ band of SF₆, using a CO₂ laser pump and a tunable diode laser probe. Power broadening of the pumped transition is observed, and a value for the transition moment μₚ = 0.3 × 10⁻⁸ cm is obtained. Off-resonant pumping of all symmetry components in the J manifold coupled to the pump laser is observed, due to a field-enhanced mixing of nearly degenerate fine-structure levels in the vibrational ground state of the molecule. From the decay of the double-resonance signals, we measure relaxation times τₚ = (24 ± 3) ns for 2-level signals and τᵣ = (43 ± 11) ns for 3-level signals, corresponding to an effective cross section of 1.5 Å². Excited-state transitions corresponding to 2ν₁ - ν₁, with J = 32 are observed. The implications for multiple infrared photon excitation models are considered.

I. INTRODUCTION

Once the collisionless, multiple infrared photons induced dissociation of molecules such as SF₆ by intense CO₂ laser pulses was found to be both an efficient and an isotope-selective process, a great deal of attention was directed toward understanding this phenomenon. Of a number of questions which have been raised about the nature of this process, one which is not yet settled concerns the nature of the initial excitation steps, that is, the route by which a molecule absorbs the first two to five photons, prior to reaching its vibrational "quasi-continuum." This problem arises because the anharmonicity of the vibration will tend to displace the (n + 1)ν₁ - ν₁ bands to successively longer wavelengths, and thus out of resonance with the single-frequency pump laser.

Several suggestions have been put forward for achieving the required anharmonic compensation, but each has been found untenable in the light of subsequent experimental developments. Bloemergen et al. initially showed that a classical, driven anharmonic oscillator could be coherently pumped, via multiphoton absorption, to the required vibrational excitation level. However, they observed a threshold for dissociation (≈ 50 kW/cm²) too low for the classical approximation to be valid. Amberzumian et al. suggested a "P-Q-R" compensation scheme, in which a single laser line pumps first a P₂(2) line in the SF₆ ν₁ = 0 band, then a Q(1)' line in the 2ν₁ - ν₁ band (which happens to occur at just the same frequency), followed by a R₁(0)' line in the 3ν₁ - 2ν₁ band, at which point the molecule is presumed to have reached the quasi-continuum. Clearly, such a coincidence of frequencies would be highly fortuitous at any one laser line, let alone applying to all the CO₂ laser lines [P(10) to beyond P₃(0)] which can be used for dissociating SF₆. Further consideration of the SF₆ ν₁ mode led to the realization that for n ≥ 2, the degenerate ν₁ levels could be split by anharmonic coupling. These splittings were calculated, and appeared to offer a nearly resonant pathway for CO₂ laser photon absorption up through n = 5. However, the calculated splittings are not consistent with recent observations on the 3ν₁ - 0 overtone absorption spectra. Recently, Ackerman and Gabrieli have suggested that Coriolis interactions in the excited vibrational levels of SF₆ produce a distribution of transition frequencies adequate to account for the observed multiple infrared photon excitation behavior. We will return to this model later in this paper.

To decide among these various models, we need some definite information on the location of levels in 2ν₁, such as frequencies of assigned transitions in 2ν₁ - ν₁. One way of obtaining such information is by means of infrared double-resonance (IDR) spectroscopy, in which the sample is pumped by a high-intensity CO₂ (or other) laser, and probed with a lower-intensity beam at another IR frequency. A variety of information can be obtained from such experiments, including:

(a) 2-level IDR, in which the pump and probe beams are at the same nominal frequency. Power broadening of the saturated transitions is observed, and a T₁-type decay time can be determined.

(b) 3-level IDR. Ground-state depletion (ESD) can be observed at frequencies remote from the pump line, providing verification of the assignments of the pumped levels. Excited-state absorption (ESA) provides direct information on the frequencies of transitions originating in the vibrationally excited state (ν₁, in this case).

(c) 4-level IDR, in which signals are observed at transitions not directly coupled to the pumping field, provides information on collisional relaxation pathways among the levels.

IDR was first carried out on SF₆ using two CO₂ lasers (Q switched and cw). A "red"-shifted transient absorption was observed, which was attributed to a superposition of absorptions from vibrationally excited levels following V→Y relaxation out of the initially pumped ν₁ level. Amberzumian et al. have supported their P-Q-R anharmonic compensation model with the observation that the absorption curve measured in Ref. 12 is nearly coincident with the curve of SF₆ dissociation efficiency vs CO₂ laser line frequency. However, the transient absorption observed in IDR corresponds...
In a much lower level of excitation than in the collision-free multiple-photon excitation experiments; the absorption profile can be well represented by that of shock-heated SF\textsubscript{6} at 550 K, while various models for the multiple-photon excitation require effective temperatures of 1700 to 2200 K.\textsuperscript{11}

The IRDR method has been extended to lower sample temperatures,\textsuperscript{11} to shorter (< laser) time scales with the use of mode-locked CO\textsubscript{2} lasers,\textsuperscript{16} and also to higher excitation levels (\(\epsilon_{\text{v}} \approx 5\)) by means of pump pulse probe pulse experiments.\textsuperscript{17} Recent experiments\textsuperscript{14} using a CO\textsubscript{2} TEA laser pump/cw CO\textsubscript{2} laser probe have extended this range to \(\epsilon_{\text{v}} \approx 19\). In all of these experiments, however, the system could be probed at only a limited number of discrete frequencies, dictated by the available CO\textsubscript{2} laser lines. To observe finer details of the transient IRDR spectrum, it is necessary to use a tunable probe source, as in the work reported here, in which the probe is a tunable diode laser.\textsuperscript{11} Similar experiments, employing a CO\textsubscript{2} laser pump source and a tunable diode laser probe source in a configuration somewhat different from that described here, have also been carried out by Moniz and Monrad at the M.I.T. Lincoln Laboratory.\textsuperscript{3,11}

II. EXPERIMENTAL

A. Instrumentation

The general scheme of the apparatus used in the experiments is similar to that described in Refs. 12 or 18, namely, a high-intensity Q-switched CO\textsubscript{2} laser beam is made to overlap with a low-intensity, tunable, cw laser beam in a sample of SF\textsubscript{6}. We measure changes in the transmittance of the cw beam which are correlated with the pump beam pulses.

The pulsed CO\textsubscript{2} laser is a spinning-mirror (150 Hz) Q-switched continuous discharge with a dispersive cavity. The 2 mJ pulses, collected from a higher order diffraction of the intracavity grating, are 400 nsec (FWHM) with a low-intensity tail extending to 1 microsec. The beam waveform was measured with a variable aperture and found to have a Gaussian profile with a width of 0.255 cm, corresponding to an effective area of 0.3 cm\textsuperscript{2}. The pulse is collected by three gold coated flat mirrors which direct it to a fourth mirror located just in front of the gas sample cell. The pulse is reflected at an angle such that the CO\textsubscript{2} laser pulse and the diode laser probe beam overlap throughout the region of the cell. The pump beam, which is counter-propagating relative to the probe beam, exits the gas sample cell at a small angle (\(\approx 1\)) with respect to the probe beam and intersects a mirror which finally directs the pump beam away from the apparatus to reduce scattered light.

The diode laser is a Laser Analytics Model SDL-30 Nd\textsubscript{3}\textsuperscript{+} element mounted in a Model TCR closed-cycle refrigeration, which is temperature stabilized to \(\pm 0.001\) °C over the operating range 14–100 K. Current to the diode is provided by an Arthur D. Little TDLS-II power supply, which is current stabilized to \(\pm 0.0001\) A over the range 0.5–2.0 A. This combination provides tunable infrared output over the range 930–980 cm\textsuperscript{-1} in a series of modes from 0.2 to 1.0 cm\textsuperscript{-1} in width, with 1–2 cm\textsuperscript{-1} gaps between modes. The modes can be shifted in frequency to a limited extent by varying the temperature set point of the closed-cycle cooler. Multimode power output is 0.1 to 1.0 mW. The linewidth was not measured directly, but is certainly far less than the Doppler width of individual SF\textsubscript{6} lines, which is \(\approx 30\) MHz, or \(0.001\) cm\textsuperscript{-1}. The diode laser mode profiles are reproducible as long as the diode is maintained at a suitably low temperature (typically 15–25 K). Since the diode power is very low, there are no saturation effects produced by the probe beam.

The diode laser radiation is collimated by a 5 cm f/1. IRTRAN\textsuperscript{5} lens and reflected through the sample cell by a gold coated mirror. Two additional mirrors direct the beam to a 25 cm f/1. paraboloidal focusing mirror and thence to the entrance slit of a Bausch and Lomb 0.25 m monochromator equipped with a 300 l/mm grating blazed at 3 \(\mu\)m and operated in third order. The monochromator is used to separate the longitudinal modes of the diode laser beam, as well as to attenuate scattered radiation from the Q-switched CO\textsubscript{2} laser. An Arthur D. Little Kg-Cd/Te infrared detector in a homemade liquid nitrogen dewar is mounted at the exit slit of the monochromator. The signal is preamplified, ac coupled to a Tektronix 1121 amplifier (gain variable from 1 to 100), and sent to a PAR Model 160 Boxcar Integrator. The Boxcar Integrator is triggered 10 \(\mu\)sec before the Q-switched laser emits a pulse. This is accomplished by an amplified signal from a photodiode positioned near the rotating mirror of the Q-switched laser such that the rotating mirror reflects the light from a small white light lamp onto the diode before achieving maximum \(Q\) for the laser cavity during its rotational cycle. The signal is sampled with a 0.5 \(\mu\)sec gate either coincident with the Q-switched laser pulse or at a selected delay following the pulse. The output of the Boxcar Integrator is coupled to the \(y\) axis of an x–y recorder (OME Corporation, Model 815 M). The x scale signal is provided by an output voltage of the diode laser power supply which is proportional to the current output to the diode laser element. For the relaxation time measurements, the Boxcar Integrator is replaced by a Biomation 620 Transient Recorder. The entire apparatus is diagrammed in Fig. 1.

B. Calibration

In working with the tunable diode laser, it is necessary to have a frequency calibration accurate to \(\pm 0.0001\) cm\textsuperscript{-1} within each individual mode. This is accomplished by measuring reference spectra along with each double resonance spectrum. To record these spectra, the diode laser beam is chopped at 100 Hz and the signal from the detector is coupled to a PAR Model 120 lock-in amplifier, and thence to the x–y recorder. Scans of SF\textsubscript{6} absorption profiles, recorded in this way, are included in the double resonance spectra shown in the following sections.

The primary frequency markers are the \(P\)-branch lines themselves of the 0001–1000 transition of "hot"
CO$_3$. The SF$_6$ absorption features in the neighborhood of these lines have all been assigned by McDowell and co-workers, for the CO$_3$ P(14), P(1a), and P(20) lines, the P(13) and P(22) lines, and in the congested region around the P(18) line, In other regions of the spectrum, we could use lines of the 00'1' - 10'0 transition in N$_2$O, or ammonia lines measured between 942 and 956 cm$^{-1}$ by Nereson. To intergrade between these discrete frequencies, we used a 1 in. solid Ge etalon with a free spectral range of 0.0499 cm$^{-1}$. Interference fringes, recorded in the same manner as an absorption spectrum, were counted to provide the frequency difference from a standard feature and a desired spectroscopic feature at an unknown frequency. Finally, a fairly extensive "map" of the SF$_6$ 10 m absorption spectrum was made available to us by Los Alamos Scientific Laboratory, from which most of the absorption features could be readily identified.

C. Artifacts

In carrying out these experiments, it is essential to keep scattered pump-beam light from interfering with the desired signals. The Q-switched CO$_2$ laser intensity is -10 kW/cm$^2$, while that of the diode laser is -9.1 mW/cm$^2$; thus, a rejection ratio of 10$^4$ between the two beams is required. This is accomplished by extensive spatial filtering, using iris-diaphragm apertures, along the beam path, by angling the cell windows to avoid direct backward reflections, and especially by using the monochromator as a very narrow-band filter to isolate the diode mode from the CO$_2$ pump line. If such precautions are not taken, a portion of the CO$_2$ laser pulse reaches the diode itself, inducing severe frequency and amplitude fluctuations in the diode laser output. Since this output passes through the SF$_6$ absorber before being detected, the resulting signal will display all of the structure of the original absorption spectrum, and can easily mask the desired double-resonance signals.

III. RESULTS

A. 2-level IRDR

The line shape of a saturated transition may be studied by tuning a probe field across a transition which is simultaneously irradiated by a pump field and monitoring the signal change of the probe. We have carried out such measurements at the CO$_3$ P(18) and P(22) lines, which pump in the P(32) and P(84) manifolds of SF$_6$, respectively. In both cases, there is a strong "hole burning," or induced transparency, in the absorption spectrum at the frequency of the pumped transition. The double resonance signal at the P(18) pump line is shown in Fig. 2. One sees, in addition to the expected saturated line, a series of weaker satellite signals to the "red" of that line. The strongest features can be identified with the other symmetry components of the P(32) manifold, which are not directly pumped by the CO$_3$ P(18) line; the reason for their appearance will be considered shortly. The addition of a foreign gas, such as Ar [Fig. 2(b)], results in enhancement of the intensity of these satellite lines, and appearance of additional, weaker signals in the P(32) manifold, corresponding to a change in $J$' of one quantum of rotational angular momentum. Further addition of foreign gas, or observation of the spectrum after a -1 usec delay, shows a residual population depletion at the pumped transition, while the rest of the rotational line structure appears to show a nonspecific, overall decrease in intensity [Fig. 2(c)].

In Fig. 3, we show the appearance of the two-level double resonance spectrum at pump laser intensities...
between 0.8 and 11.2 kW/cm². Two observations are especially noteworthy: first, the "satellite structure" appears rather abruptly between -1 and -3 kW/cm² applied intensity; second, the strong central feature appears to broaden as the intensity is increased. We shall return to the first point in the ensuing discussion.

The line width at half-height of a power-broadened transition is given by

\[ \Delta \nu_{1/2} = \frac{1}{\pi} \left[ 1 + \frac{\mu_1^2 \xi_1^2}{2} \right]^{1/2} \]

where \( \mu_1 \) is the transition dipole moment and \( \xi_1 \) is the electric field associated with a beam of intensity \( I \).

If the Rabi frequency \( \frac{\mu_1 \xi_1}{\hbar} \) is much larger than \( \left( \frac{\Delta \nu_{1/2}}{2} \right) \), Eq. (1) may be simplified to

\[ \Delta \nu_{1/2} = \frac{\mu_1^2 \xi_1^2}{2 \pi \hbar} \]

If we make the further reasonable assumption that \( T_1 = T_2 \), we obtain

\[ \Delta \nu_{1/2} = \frac{\mu_1^2 \xi_1^2}{2 \pi \hbar} \]

For these, the measured half-width should be proportional to the square root of the intensity. A plot of these quantities is shown in Fig. 1; the expected relationship appears to be reasonably well fulfilled. A theoretical estimate of the proportionality factor, obtained by using the value of \( \mu_{11} = 0.388 \times 10^{-14} \text{ esu cm} \), is \( \Delta \nu_{1/2} \propto I^{1/2} \), which compares favorably with the measured slope of 74 MHz/(kW/cm²)⁻¹/².

Similar values are also obtained in the two-level double resonance experiments at the CO₂ P(12) and P(22) lines. At an applied intensity of 23 kW/cm², at which single-frequency multiphoton dissociation becomes appreciable, Eq. (3) would predict a power-broadened "hole" width of 11 GHz or ~3 cm⁻¹; at 1 GW/cm², which is attainable with focused TEA laser beams, the width would increase to ~2.3 cm⁻¹, which is an appreciable fraction of the inhomogeneously broadened infrared band.

Figure 5 shows the time development of the double resonance signal during and immediately following the pump laser pulse. For this experiment, the boxcar integration gate was set at 100 nsec; the "zero delay"
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The time development of the strong saturation signal is shown in Fig. 6. From separate determinations at 0.05 to 0.12 Torr SF₆, we obtain a value for the relaxation time $\tau_R = (24 \pm 3)$ ns Torr.

Deuterium resonance spectra were also recorded in the presence of He, Ar, and CH₃F as added buffer gases; the results are discussed below, in Sec. III C.

Three-level double resonance signals were observed upon pumping SF₆ with the CO₂ $P(14)$, $P(16)$, and $P(18)$ laser lines. The $P(16)$ line pumps in the dense $Q$ branch of the molecule, and produces a complex IRDR spectrum covering the $R(45)$ through $R(52)$ lines (this is shown in Fig. 8); $Q$-branch lines corresponding to these $J$ values may be found within a 280 MHz of the CO₂ pump line, in agreement with the power-broadening arguments presented earlier. A much simpler DR spectrum is obtained on pumping with either the $P(14)$ or $P(18)$ CO₂ lines; an example of the former is shown in Fig. 7. The strongest feature corresponds to the $A^1_1 - F_1^1 + F_2^1$ symmetry components of the $P(28)$ manifold at 946.308 cm⁻¹, resulting from ground-state depletion of the $A^1_1 + A^3_1 + F_1^1 + F_2^1$ symmetry feature of the $R(28)$ manifold, which is pumped by the CO₂ laser $P(14)$ line at 949.479 cm⁻¹. As in the case of the two-level double resonance, the other symmetry components of the $P(28)$ manifold appear as satellite structure around the main line. The strong IRDR signal corresponding to the $A^1_1 - F_1^1 + F_2^1$ components of the $P(30)$ manifold. The reason for this is quite straightforward: the $R$ branch transitions couple only to the $F^1$ levels, while the $P$ branch transitions couple only to the $F^2$ levels. Thus, the $R(28)$ and $P(30)$ manifolds possess no upper level in common, and no 3-level IRDR signal of this type should be expected.

The relaxation time of the 3-level IRDR signal was measured in a manner similar to that described in the previous section. The measured value of $\tau_R$ was $(43 \pm 11)$ ns Torr; this is significantly longer than that measured for the 2-level IRDR signal. The reason for this difference will be discussed shortly.

**FIG. 4.** Plot of power-broadened line width (FWHM) of two-level double-resonance signal vs square root of pump laser intensity.

scan is coincident with the leading edge of the pump laser pulse, and successive scans are incremented by 100 ns each. Note that the satellite structure appears as soon as the pump pulse reaches an appreciable fraction of its peak intensity. The time development of the strong saturation signal is shown in Fig. 8. From four separate determinations at 0.05 to 0.12 Torr SF₆, we obtain a value for the relaxation time $\tau_R = (24 \pm 3)$ ns Torr.

The relation time of the 3-level IRDR signal was measured in a manner similar to that described in the previous section. The measured value of $\tau_R$ was $(43 \pm 11)$ ns Torr; this is significantly longer than that measured for the 2-level IRDR signal. The reason for this difference will be discussed shortly.

**FIG. 5.** Development of the two-level infrared double resonance signal to 0.06 Torr SF₆ as a function of time. In the "zero-delay" scan, the 100 ns sampling gate is set to the leading edge of the CO₂ laser pulse. The gate is then incremented by 100 ns intervals in the successive scans between 1 and 10 µsec. The small arrow in the lower absorption trace indicates the position of the CO₂ $P(16)$ line, as in Fig. 4.
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FIG. 8. Relaxation of two-level double resonance signal in 0.083 Torr SF$_6$. Upper trace: CO$_2$ laser pulse profile. Lower trace: diode transmission signal. The relaxation time (470 nsec) is obtained by fitting to the signal at times longer than 0.9 µsec, i.e., after the end of the pump pulse.

FIG. 9. Three- and four-level infrared double resonance spectra. The bottom curve is a diode laser absorption spectrum of 0.08 Torr SF$_6$ in the $R(45)$-$R(52)$ region. Above this is an IRDR scan in the same spectral region, pumping with the CO$_2$/P(18) line at 947.78 cm$^{-1}$. The top three traces are the same region, pumping with the CO$_2$/P(18) line at 947.78 cm$^{-1}$. Middle to top: 0.08 Torr SF$_6$ alone; 1 Torr CHF$_3$ added; and 1 Torr He added. All spectra taken with 0.5 µsec gate coincident with the pump laser pulse.

In addition to ground-state-depletion signals, excited-state-absorption signals may be seen arising from pumped levels in $v_3$, corresponding to $2v_2-v_3$ transitions. As an example of such signals, observed in this work, may be seen in the third trace in Fig. 8. Two new absorption features are observed at 950.300 and 950.060 cm$^{-1}$, on pumping with the CO$_2$/P(18) line at 947.780 cm$^{-1}$.

C. 4-level IRDR

When collisions transfer populations from rotational levels directly pumped by the CO$_2$ laser to others, not directly coupled to the pump field, four-level double resonance spectra may be observed. In general, these spectra are more complex than the 2- and 3-level IRDR signals. Examples of collision-induced structure may be seen in Figs. 2 and 7; a clearer example is shown in Fig. 8, in which we observe in the $R(45)$-$R(52)$ region, while pumping with the CO$_2$ laser P(18) line. This line pumps $J'=33$ (and some 32) in SF$_6$, and no 3-level IRDR signals are observed in a low-pressure SF$_6$ sample. Addition of He produces little additional signal, but addition of a similar amount of CHF$_3$ produces numerous IRDR signals, both ground-state depletion and excited-state absorption. This implies collisional changes in $J$ of 10 to 15 quantum units of angular mo-
IV. DISCUSSION

The principal observations from this work are: Off-resonant symmetry components of a given J level are pumped, at least to some extent, by a laser: line resonant with only a single component, the spectroscopic assignments in the SF₄ ν₁ - ν₂ band are confirmed in detail, and several lines from the 2ν₁ - ν₂ band are observed; and collisional relaxation times for the laser-pumped J levels are determined, with no apparent restrictions on symmetry changes in such collisions. We will discuss each of these points briefly, and conclude by considering the implications for our understanding of multiple infrared photon dissociation processes.

A. Coupling of ground-state manifolds: Collision or field induced?

As can be seen in Figs. 2, 3, and 5, the 2-level IRDR hole-burning signal is accompanied by satellite structure corresponding to the entire symmetry manifold of a given J level. This structure is essentially fully developed after 100 nsec, at an SF₄ pressure of 0.08 Torr (see Fig. 5). If collisional relaxation within the J manifold were responsible, the cross section for such collisions would have to be in excess of 1100 Å². This is a situation reminiscent of that in Ref. 16, in which collisionless relaxation processes had to be invoked to account for the rapid (-nsec) decay of the pumped levels. Unlike Ref. 16, however, we are not in a regime of a high density of states, so that a purely intramolecular mechanism can be ruled out. Instead, we consider the mixing of near-degenerate symmetry components in the ground vibrational state, brought about by field-induced perturbations associated with the pump laser field.

The splittings in the ground-state J manifold are of the order of a few MHz, while the power broadening at 1 kW/cm² and above is several hundred MHz (see Fig. 3). Thus we expect these components to be strongly mixed by second-order Stark effects. The dominant mixing will be between sublevels of the same symmetry designation \( A_3 \). From Fig. 3, we see that the satellite structure appears rather sharply between 0.8 and 3.7 kHz, a range over which the Rabi frequency increases from ~100 to ~200 MHz (see Fig. 4). At the lower end of this range, the pump laser field interacts only with the \( P(33) A_3 \) line, while at Rabi widths of 200 MHz and above, \( P(33) F_3 \), \( F_2 \), \( F_1 \), and \( E' \), in addition to \( P(31) F_3 \), features, become involved. Thus, all symmetry components of the \( J = 33 \) manifold (and some in \( J = 32 \)) become accessible via the mixing process. The \( A_3 \) component is not coupled in this mechanism, but this would not be noticed, since a pure \( A_3 \) line does not appear in the spectrum.

The matrix elements appearing in the mixing coefficients are off-diagonal in the pure rotational angular momentum operator \( R \) by a one quantum unit. These matrix elements are also responsible for the "weak (J-nonconserving) transitions" in SF₄, which have been suggested as an important part of the multiple photon absorption process. Calculations of the mixing coefficients, and comparison with these experimental results, which are currently in progress, should provide information on both the centrifugal splittings in the ground-state rotational manifold and on the strengths of the weak transitions. More exact calculations of the details of the power-broadened off-resonant line shapes will require the methods developed by Mollow and by We et al. 6

B. SF₄ ν₁ spectroscopy

In the case of SF₄, a thorough analysis of the vibration-rotation spectrum is available, so that the 2- and 3-level IRDR spectra serve merely to confirm the assignments, as well as to validate the method itself. From the excited-state-absorption transitions (Sec. III B, Fig. 6) we may obtain at least an estimate of the 2ν₁ - ν₂ band profile. Pumping at \( P(18) \) produces as apparent A-branch line at ~950.5 cm⁻¹; the 2-level IRDR (Sec. III A) confirmed that we are pumping in the \( J'' = 33 \) level. We consider a highly simplified approximation in which we treat the 2ν₁ - ν₂ band as having a
A single origin at 945.5 cm\(^{-1}\), an effective Coriolis constant \(\xi_s\) and a rotational constant identical to that of the fundamental. Considering the line position of the R(32) transition at 950.5 cm\(^{-1}\), we obtain from the line position equation for a spherical top,\(^{26}\)

\[ B(1 - \xi_s)^2 + (1 - \xi_s)B = \Delta v, \]

where \(\Delta v = 5\) cm\(^{-1}\) is the displacement of the R(32) line from the assumed band center for the 2-vB transition, \(J = 2\) is the rotational quantum number, \(\xi_s = 0.67\) is the Coriolis constant for \(\nu_1\), and \(B = 0.09\) cm\(^{-1}\) is the rotational constant of \(\nu_1\). Substituting these values into Eq. (4) we obtain \(\xi_s = 0.41\). Since \(B_{eff} = B(1 - \xi_s)\), the 2-vB band would be much wider than the fundamental. Clearly, a much larger number of excited-state transitions will have to be identified before any more detailed analysis can be attempted.

### C. Collision-induced relaxation

These experiments represent the first direct observation of relaxation from individual rotational levels in a spherical top. The standard technique of microwave double-resonance spectroscopy\(^{27}\) cannot be applied to such molecules, since they do not possess a permanent dipole moment\(^{28}\); laser-excited infrared fluorescence\(^{29}\) is also not applicable, since the intensity-limited resolution is insufficient to resolve rotational features.

The exponential decay constant for the double-resonance signals was found to be (25 ± 3) nsec Torr for the 2-level IRDR (Sec. III A), but (43 ± 11) nsec Torr for the 3-level IRDR (Sec. III B). The reason for this difference may be understood by reference to Fig. 10. First, it is necessary to note that the observed double-resonance signal is proportional to the difference between the transmitted diode intensity at the observation time \(t\) and that at a time \(\tau\) when the intensity is no longer changing. The former is proportional\(^{30}\) to the instantaneous population difference \((v_0 - v_1)\) between ground and excited vibrational states, respectively, while the latter is proportional to the equilibrium value of this difference, \(v_0 - v_1\). Thus, the observed signal \(S_0(v_0 - v_1) - (v_0 - v_1)\). The relaxation behavior will be given by

\[
\frac{dS_0}{dt} = \gamma_2 \left[ (v_0 - v_1) - (v_0 - v_1) \right] \frac{dF_0}{dt} - \gamma_1 \frac{dF_1}{dt} = -\gamma_1 S_0 \frac{dF_1}{dt} + \gamma_2 S_0 \frac{dF_0}{dt} \]

\[ \frac{dF_0}{dt} = -\gamma_1 S_0 \frac{dF_1}{dt} + \gamma_2 S_0 \frac{dF_0}{dt} \]

where \(\gamma_0\) is the relaxation rate in the ground vibrational state, \(\gamma_1\) in the excited vibrational state, and \(\gamma_2\) is the observed phenomenological relaxation time. If the 3-level system we are observing [case (ii)] is fully saturated, then \((v_0 - v_1)_{sat} = (v_0 - v_1)_{eq}\) and

\[ \frac{1}{\tau} = \gamma_0 + \gamma_1 \]

If we take \(\gamma_0 = \gamma_1 \gamma_2 / \gamma_0\), as Moulton's experiments indicate.\(^{30}\) On the other hand, in the 3-level system [case (i)]

\[ \frac{1}{\tau} = \gamma_0 \]

Thus, even though the rate of gas-

\[\text{J. Chem. Phys., Vol. 77, No. 8, 1 November 1979}\]
Stirring SF₆-Ch₂F collisions (1 x 10⁶ sec⁻¹ at 300 °K, 1 Torr) in half of SF₆-He collisions (2 x 10⁶ sec⁻¹), energy transfer in the SF₆-He mixture is considerably less efficient than in the SF₆-Ch₂F mixture. The SF₆-SF₆ or He-SF₆ collision interaction can be characterized by a dispersion force with a 1/r³ dependence, where r is the distance between collision partners. The collision interaction for CH₂F-SF₆ is expected to be dominated by a dipole-induced dipole force with a 1/r⁵ dependence. The longer range interaction of the CH₂F-SF₆ collision interaction is expected to be more efficient in energy transfer than the He-SF₆ collision interaction, as is evidenced by these results.

At longer times (Fig. 9), much of the detailed spectral structure is lost, indicating that all probed levels are nearly equally involved in the relaxation process.

D. Implications for multiple infrared photon absorption processes

The results obtained in this work can help to clarify the mechanism of the initial absorption steps in the multiple infrared photon induced dissociation process. The model which above most closely to our observation is that of Ackerhalt and Galbraith, in which rotational compensation is the dominant mechanism of overcomin superharmonicity. Field-induced mixing of symmetry components within a J manifold appears to make an important contribution to initiating multiple absorption ladders, at least in spherical-top molecules. It is worth noting that we did not observe any "weak (A=0) transitions," which have been proposed by Knyazev et al., as a way of obtaining superharmonicity.

Power broadening of the absorption line shape can be very important in multiple infrared photon excitation of light molecules, in which the absorption spectrum is sparse relative to the CO₂ laser line shape. This will lead to the nonlinear intensity dependence of energy deposition and dissociation yield observed in such systems as vinyl chloride. This effect may combine with pressure broadening to cause a significant increase in yield with added buffer gas pressure, e.g., in vinyl fluoride and CDF₆. We plan to explore these effects in greater detail, using diode-laser induced laser double resonance. The calculated rotational relaxation effects observed in this work will also contribute importantly to multiple-photon absorption via parallel excitation ladders.

The BDR spectra confirm in detail the assignments made for the well-studied SF₆, fundamental of SF₆. For gas which are not as well interpreted, however, this method will be a useful technique in carrying-out the analysis. For example, from the 3-level BDR signal (Sec. III B), we obtain a measurement of the J=23 combination difference Δv(J−P)=946.479 -946.308=0.171 cm⁻¹, from which a value for B₁ can be obtained directly. For measurements in excited vibrational states, the BDR technique is essential. In this connection, use of a tunable infrared pump, instead of a CO₂ laser at fixed frequencies, would be particularly desirable.

ACKNOWLEDGMENTS

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F.1 Introduction

In recent years, the low cost of laboratory microprocessors and minicomputers has enabled many laboratories to obtain digital processors for signal recovery and analysis and for computation. Concurrently, transient digitizers have become popular, but leave the experimenter the task of linking the digitizer to his processor. Although successful interfacing designs have been reported [F-1, F-2] they are not straightforwardly adaptable to other processors or digitizers. In this paper we report interface designs suitable for linking many different Biomation transient recorder models to the Digital Equipment Corporation PDP 8 and LSI 11 families. Specifically, our devices have linked a Biomation Model 820 to a MINC (LSI 11/2) and a PDP 8/L processor.

A block diagram for the interfaces is shown in Fig. F-1. In both cases, most of the interface is contained on a single general-purpose interface card available from DEC. A few extra gates are necessary to adapt the general interfaces to the 820. In both cases a multiconductor ribbon cable connects the 820 to the interface, which is located in the processor cabinet.
F-1. Block diagram for Biowation 820 interfaces.
Since the 820 and other Biomation models use only two active "handshaking" signals, COM and FLG, to gate the transfer of digitized records to the computer, these interfaces should be useful for a variety of transient recorder models. The present systems also provide for computer control of the transient recorder, or computer-to-820 datum transfer, although maximum transfer rates are attained when the digitizer runs in AUTO DIGITAL, or automatic transfer mode.

F.2 MINC Interface

The DRV11-B DMA interface used for the Biomation-MINC link required three extra TTL chips to be mounted on the interface card itself. One, a 74121 monostable, was placed in convenient predrilled holes. The other two, a 7410 NAND buffer and a 74367 tri-state buffer, were glued to the back side of the interface card. The only other modification of the DRV11-B board was to remove the copper artwork connecting pins K and L of connector J2 (output connector) so that pin K could be used to route the signal COM from the extra 74367 chip to the 820. The schematic for the entire interface is shown in Fig. F-2.

Communication between the DRV11-B and the 820 is accomplished via a 48-conductor 26 AWG ribbon cable approx. 26 meters in length. Every other wire in the cable is ground
F-2. Circuit diagram for MINC interface. Not shown are the following constant logic levels: Hi to 820 pins 19, 24, 25; J1 pins J, J2 pins F, J, T. Lo to 820 pins 14-16, 20-23; J1 pins K, R, BB, CC; J2 pins D, N, DD-VV.
to minimize crosstalk. Voltages necessary to specify constant logic levels at the DRU11-B were routed from the 820 connector through the cable to the DRU11-B connectors. Specifically, the DMA interface was wired for burst mode or synchronous transfer to insure maximum transfer rates, although single cycle or asynchronous transfer was also used successfully. Thus, once the 820 initiates transfer, all data are transferred at the maximum rate, which is determined by the MINC bus cycle time. Also, logic specifying DATO or DRU11-B to 820 transfers was hard wired, even though some exchanges may actually pass Input Control data to the 820, as explained below.

Operation of the interface is straightforward. First, under software control, the word count register (WCR) in the DRU11-B is loaded for the desired number of data words to be transferred. For Input Control or Output Status transfers, only one word is transferred. For transfer of a digitized record, any number up to 2K words can be chosen. Next the bus address register (BAR) is loaded with the location to which transfer is desired in MINC memory. The bit pattern corresponding to the desired Biomation 820 operator/operand command is then placed in the DRU11-B output data buffer register (ODBR), where it will stay throughout the data transfer. Note that if Bit 12 is hi in the ODBR, the 820 will interpret the command as an Input Control command even though the DRU11-B has been wired for 820-to-DRU11-B data transfers. Finally, the GO bit in the control/status register (CSR) is
written hi, activating the interface.

As shown in the timing diagram, Fig. F-3, when the GO bit turns hi, the READY line goes lo, asserting COM (10). The 820 interprets this as a command transition and interprets the command word in the ODBR. FLG goes lo while the 820 is busy, and when it rises the monostable (121) is triggered. On the rising edge of the monostable CYCLE REQ pulse, the DRV11-B latches data from the 820 into the input data buffer register (IDBR). Busy goes hi, forcing COM hi, and a DMA cycle is performed to pass the data word to MINC memory. If more than one word is to be transferred, BUSY goes lo at the end of the DMA cycle while READY stays lo, thus causing another COM pulse and subsequent data transfer. After the required number of words are transferred, READY goes hi, BUSY remains hi, and the DRV11-B makes an interrupt request if the interrupt enable bit in the CSR is on. Using a program similar to the one below, data transfer rates of greater than 58 full 2K records/sec was accomplished with an 820 recording timebase of 8.05 microseconds:

```
MOVBINTH,124 ; LOAD INT VECTOR HANDLER
MOVB#4000,WCR ; LOAD WCR FOR FULL REC XFER
MOVB#BUF,BAR ; DATA STASHED IN BUF BUFFER
MOVBCDAT,ODBR ; LOAD DATA OUT COM INTO ODBR
MOVBGO,CSR ; TURN DRV11-B ON
WAIT ; WAIT FOR INTERRUPT=DONE
RTS PC ; INTERRUPT OCCURS
INTH: ; EXIT FROM SUBROUTINE
RTI ; NO 'HANDLING' NECESSARY
CDAT: .WORD 4000 ; CATA OUT COMMAND
GO: .WORD 101 ; DRV11-B GO COM W INTERRUPT
BUF: .BLKW 4000 ; RESERVE 2K WORD BUFFER
```
F-3. Timing diagram for DRV11-B burst mode word transfers.
No errors in data transfer were detected even though the ribbon cable exceeds the recommended maximum length of 50 feet (17 meters). Programs similar to the one above have been written as generalized FORTRAN-callable subroutines.

Although it was not implemented in our interface, the highest three bits of the ODBR may be used to address more than one 820 unit. In this manner a single DRUii-B could transfer data from several units, one at a time, via a parallel bus cable connecting them.

F.3 PDP 8/L Interface

Unlike the MINC interface, the device chosen to effect transfer from the 820 to our PDP 8/L was a program data transfer module M735. This device is considerably slower than a DMA interface, but for the PDP 8 family, a DMA interface is not available on a single card. Thus, for simplicity in circuit design and ease in programming, a wordwise program transfer module was chosen.

The schematic for the 820 to 8/L link is shown in Fig. F-4. Data from the M735 output data buffer (ODB) is routed through OC inverters with resistive pullup to a cable identical to the one used for the MINC link. The lowest eight bits of the ODB are connected in parallel with the corresponding bits in the input data buffer (IDB) for half-duplex operation. Other extra logic elements create
F-4. Circuit diagram for PDP 8/L interface. Not shown are the following constant logic levels: Hi to 820 pin 23. Lo to 820 pins 14-16, 19-22, 24, 25.
F-5. Timing diagram for program data transfers using the M735 interface on the PDP 8/L.
command pulses and provide for sensing FLG. Constant logic levels are implemented by daisy-chain wiring in the 820 connector plug and at the wire-wrapppable connector block in the 8/L cabinet where the M735 and other modules are inserted.

Three events, independently specifiable by the lowest three bits in the IOT microinstruction, can occur in one program data transfer cycle, as shown in Fig. F-5. At IOP1, the ODB is loaded from the accumulater (AC). IOP2 triggers a 74121 monostable, which is sent to the 820 as a command pulse. The monostable times out after IOP4, when data can be strobed through the input data buffer (IDB) into the AC.

Any combination of IOPn events can be chosen to occur in the same instruction. For Output Status operations, all three events are chosen; at the end of the IOT cycle the AC contains the eight bit status word from the 820. For Input Command operations, only IOP1 and IOP2 are chosen.

Because the operator/operand structure of the 820 requires 13 bits and the 8/L is a 12-bit processor, an extra bit is needed to specify whether Input Control or Output Status is desired. This bit is Bit 9 in the IOT instruction, which specifies whether or not an IOP4 transfer will occur. It is available on the PDP 8 bus as BMB9(1). Thus Bit 9 in the IOT microinstruction is set for Output Status, an left off for Input Control.

This arrangement works well for all operations except
DATA OUT, for which some additional software scale timing must be considered. Once the 820 has been placed in Digital Output mode by the 8/L and the first DATA OUT operator applied, a period of time passes before the 820 produces the first datum. The program can sample FLG until it goes hi, signaling the readiness of the 820. Data can then be strobed out of the 820 under program control without further delay at maximum rate, which is determined chiefly by the software routine execution time. Using a program similar to the one below, data transfer rates of about 10 full 2K records/sec was effected using a recording timebase of 0.05 microseconds on the 820:

```
TAD TRDATC / GET DIGITAL OUT COMMAND
6373 / GIVE TO 820; M735 IN LOC 37
TAD N2K
/ GET NUMBER -2K FOR FULL RECORD XFER
DCA TRCNTR / DEPOSIT IN COUNTER
DCA 10 / CLEAR AUTOINCREMEN REG 10;
/ DATA BEGIN IN LOC 8, DATA FIELD 1
TAD TRDOUT / GET DATA OUT COMMAND
6373 / GIVE FIRST DATA OUT TO 820
6371 / IS 820 READY?
JMP -.1 / NO -- ASK AGAIN
CDF1 / YES - CHANGE TO DATA FIELD 1
FTR5A, 6376 / TAKE THIS DATA WORD
DCA I 10 / DEP IN CURRENT LOC, INC 10
IS2 TRCNTR / TAKEN ENOUGH WORDS?
JMP FTR5A / NO -- GO BACK FOR ANOTHER
CDF0 / YES - RETURN TO DATA FIELD 0
TAD TRDAT2 / GET TRUNCATE DIGITAL OUT COM
6373 / GIVE TO 820
JMP I EFUN3I / SUBROUTINE EXIT
TRDATC, 3420 / CONSTANTS IN OCTAL; DIG OUT
N2K, -4000 / =-2048 DECIMAL
TRCNTR, 0 / WORD TRANSFER COUNTER
TRDOUT, 4000 / DATA OUT COMMAND
TRDAT2, 3401 / TRUNCATE DIGITAL OUT COM
```

F.4 IMPLEMENTATION
Successful implementation of this digital signal recovery system has been reported in double resonance spectroscopy experiments. The curious experimenter is invited to read references [F-3] and [F-4] for further details.

F.5 Acknowledgment

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In this Appendix, programs in machine language (PAL-III for the PDP-8/L and MACRO-11 for the MINC) for use with the Biomation 820 interfaces described in Appendix F are listed. Also included are two files used to prepare this thesis.

FORTRAN callable MACRO subroutines are simple to construct. Arguments are passed from the MAIN program to the subroutine using R5. When control reaches the subroutine, R5 points to a list in core. The first word on the list is the number of arguments in the subroutine CALL statement. The next word in the list is the address of the first argument; the next word is the address of the second argument, etc. Once the MACRO subroutine has been typed in, it is compiled with the RT-11 MACRO command. The OBJECT file created can be directly linked to a compiled FORTRAN program.

In FOCAL the arrangement is more complex. A version of 4K FOCAL called "FOKAL for TR" has been produced which includes a PAL-III function FCOM for communication with the 820. To load the entire package, one must first load the FOCAL and FOCAL modifications portion of the FOKAL for TR tape, then start at address 200. After the initial dialogue the * appears. Loading the FCOM function can then be done in the same manner as loading FOCAL. Routines for running the ARDS can be loaded optionally. Finally, FOCAL must be
restarted at location 200 as usual.

Since the FCOM function accepts only one record from the 820, recovery of many records may be slow. Another function, FLOG for TR, was written to maximize the transfer rate between the 8/L and the 820. This function can be overlaid into FOKAL for TR; it uses the space normally occupied by the FLOG function. Several features available using FCOM are not available using FLOG, so that it is recommended that if FLOG for TR is needed, FCOM should also be loaded.

FOKAL reserves the higher 4K of the 8K 8/L memory for storing data from the 820. Two words are used for one "cell", or 24 bits per cell. Since the precision of the 820 is eight bits, \(2^{16}\) or 64K records can be accumulated with no loss of precision. The 4K words of memory used for storing the 2K data cells are unavailable for use as program space, so that program space is considerably smaller than for 8K FOCAL. When the ARDS routines are loaded, program space becomes very small.

The following are brief descriptions of the programs listed in this Appendix:

TR1.MAC - MACRO subroutine for taking one variable length record from the 820. CALL TR1(NCELLS,NREC(I),ISTAT) performs a one record transfer from the 820 to the MINC. The transfer occurs when the status of the 820 equals ISTAT. The transfer of NCELLS individual points is made into consecutive words in
core starting with NREC(I). NREC should be a regular FORTRAN integer vector.

STATUS.MAC - MACRO subroutine for recovering the status of the 820.

USETR1.FOR - FORTRAN example of the use of STATUS and TR1.

OUTPUT.BAS - program used under MINCSYS to print this thesis ON the LA34 DECTRITER IV.

RUNCOM.TXT - command file for RT11 RUNOFF program provided by DEC. RUNOFF is a text formatting program which reads a text file which contains original text and commands, and outputs a finished document. A typical command to RUNOFF would be:

*SY1:CHAP3.DOC<RUNCOM.TXT,CHAP31.TXT,CHAP32.TXT/F

FCOM - function for transient recorder communication to the B/L. FCOM us called from a FOCAL program as follows:

FCOM(1,X) returns value of cell X
FCOM(2,X,Y) sets cell X to the value Y
FCOM(3,X) sends a COMMAND the 820 whose Input Control Command decimal value is X
FCOM(4,X) returns status of 820 as requested by the Output Status Command whose decimal value is X
FCOM(5,X,Y) takes X data points from the 820 and
adds then into consecutive cells starting with cell Y

FLOG - fast 820 interface function.

FLOG(A,B,C,D) takes C records with A data points per record from the 820. Each record is added into consecutive cells starting with cell B. D is the "ready" status of the 820.

PEAKAVG - FOCAL program illustrating the use of FCOM.

This program takes 400-cell records from the 820. In each record, the peak of the signal is found. If the peak value exceeds a minimum value M, it is averaged until C peaks above the minimum are recorded.
TR1, MAC
.TITLE TR1 QUICKIE 820 RECORD TAKER ; TAKES VARIABLE LENGTH RECORD ONCE ; WHEN 820 IS 'READY'
;
DWCR = 172410 ; WORD COUNT REGISTER
DBAR = 172412 ; BUS ADDRESS REG
DCSR = 172414 ; CONTROL/STATUS REG
DIDBR= 172416 ; INPUT DATA BUFFER READ ONLY
DDDBR= 172416 ; OUTPUT " " WRITE ONLY
;
DIV = 124 ; INTERRUPT VECTOR
;
TR1: ADD #6,R5 ; MOVE TO 3RD ARG
MOV CSTAT,DODBR ; LOAD STATUS COMMAND
MOV #INTH,DIV ; SET INT ADDRESS
CLR DIV+2 ; NEW PSW = 0
TRY:
CLR R1
CLR BUF2 ; CLEAR PREVIOUS TRY
MOV #BUF2,DBAR ; LOAD BUS ADDR
MOV #-1,DWCR ; 1 WORD TRANSFER
MOV GO, DCSR ; LET'S HAVE IT
W3:
NOP
NOP
NOP
NOP
NOP
NOP
NOP
TST R1 ; STATUS IN YET?
BEG W3 ; IF NO, WASTE TIME
CMPB @(R5),BUF2 ; SAME AS WANTED STATUS?
BNE TRY ; ASK AGAIN IF NO
SUB #4,R5 ; RESTORE POINTER TO 1 ARG
;
TAKE: MOV @(R5)+,R1 ; GET RECORD LENGTH
NEG R1 ; FORM NEGATIVE
MOV R1,DWCR ; LOAD WORD COUNTER
CLR R1 ; CLEAR SWITCH
MOV (R5),DBAR ; MOVE LOCATION TO BUS ADDR
MOV CDAT,DDBBR ; LOAD DATA OUT COM
MOV GO,DCSR ; LET IT RIP
W2:
TST R1 ; BACK IF NOT
BEG W2
;
INTERRUPT OCCURS
;
RTS PC ; GO HOME AFTER SHORT WAIT
;
INTH: INC R1
RTI ; POP PSW, PC
;
BUF1: .WORD 0
BUF2: .WORD 0
CSTAT: .WORD 3400 ; STATUS COMMAND
CDAT: .WORD 4000  ; DATA OUT COMMAND
CSTOP: .WORD 13401  ; STOP DATA
GO: .WORD 101  ; DRV11-B GO COMMAND WO INT
.END

 STATUS.MAC

.TITLE STATUS FOR GETTING BIOMATION STATUS
;
WCR = 172410
BAR = 172412
CSR = 172414
DBR = 172416
DIV = 124
;
STATUS::
TST @R5+  ; MOVE OVER OARG
MOV CSTAT,DRB
MOV #INTH,DIV
MOV #BUF2,BAR
MOV #-1,NCR
MOV GO,CSR
TST R5
TST R5
TST R5
TST R5
TST R5
TST R5
MOV BUF2,@R5
RTB PC
;
INTH: RTI
;
BUF2: .WORD 0
CSTAT: .WORD 3400
GO: .WORD 101
.END
USETRI.FOR
C    USETR1 -- PROGRAM TO USE MACRO ROUTINE TR1
C    30 JAN 80 BY CHRIS REISER
C
INTEGER NEWREC(2048)
C    NEWREC FOR NEW RECORDS, ACCUMULATED INTO IACC
C
CALL STATUS(ISTAT)
   TYPE 102, ISTAT
6   ACCEPT 102,NSHOTS
102 FORMAT (16)
C   ACCEPT 10 RECORDS
C
DO 10 NSHOT=1,NSHOTS
   CALL TR1(2048,NEWREC(1),ISTAT)
C   TAKE 2048 CELLS FROM 820 (THE WHOLE RECORD), PUT THEM
   IN CONSECUTIVE MEMBERS OF NEWREC STARTING WITH
   NEWREC(1), WHEN 820 HAS STATUS OF ISTAT
C
10 CONTINUE
C   USER CAN DO ANYTHING WITH DATA HERE
C   OR GO BACK FOR MORE
C
   GOTO 6
101 FORMAT (10I9)
END
FLAG for TR

5040

FLAG, N3P /NAST TRANSIENT RECORDER MUNCTION
/10.78 BY C REISER
INT /# DATA
CIA
DCA NDATA
PUSHJ
EVAL-1
INT /CELL 0
CIA
DCA N3P /NAST TRANSIENT RECORDER MUNCTION
PUSHJ
EVAL-1
INT /# RECORDS
CIA
DCA RCNTR /RECORD COUNTER
PUSHJ
EVAL-1
INT /TR READY STATE
CIA
DCA NRDY
SETUP, TAD NDATA
DCA DCNTR /DATA COUNTER
TAD FCCELL
DCA 10
TAD 10
DCA 11
ASK, TAD STASK
6377
TAD NRDY
SZA CLA
JMP ASK
TAD TRDATC /HERE WHEN READY
6373 /START DATA OUT
TAD TRDOUT
6375 /LOAD BUFFER
6371
JMP -1 /STREAD TILL FLAG
CLA CLL
CDFI
REC, 6376 /TAKE DATUM
TAD I 10
DCA 1 11 /ADD IN
TAD I 10 /HORD
SZA
IAC CLL /INC IF ONLY
DCA 1 11
ISZ DCNTR
JMP REC /BACK TILL EOR
CDFO
TAD
6373 /TURN OFF DATA
ISZ
JMP
JMP 1 EFUN31 /BYE
/
/
NDATA, 0
N3, -3
FCELL, 0
NRDY, 0
RCNTR, 0
DCNTR, 0
STASK, 3400
TRDATC, 3420
TRDOUT, 4000
D0FF, 3401
//
/
EFUN31=0136
CDFO=6201
CDF1=6211
PUSHJ=4540
INT=JMS 1 0053
EVAL=1613
/
$
FTRR, /FUNCTION FOR TRANSIENT RECORDER
/10.77 BY CHRIS REISER
INT /MAKE 1ST ARG INT
PIUSHA /STORE
PIUSHJ
EVAL-1 /GET NEXT ARG
CLA
P0PA /RECOVER FCN #
TAD FTRA /ADD JMP 1
DCA +1 /SET UP JMP
0 /THIS WILL BE A JMP 1
FTRA, JMP 1 . /JMP TO LIST
FTR1
FTR2
FTR3
FTR4
*TR5
FTR3, INT /GET DATUM
6373 /GIVE TO TRANSIENT REC
JMP 1 EFUN31 /AND THATS ALL
FTR1, JMS FTRADD /RETURNS CELL X ADD
CDF0=6201
CDF1=6211
CDF1 /CHANGE DF
DCA TRCURAD
TAD I TRCURAD /PUT CUR ADD & TAKE L0RD
CDF0
DCA L0RD /PUT IN L0RD
CDF1
TAD I TRCURAD /PICK UP H0RD
CDF0
DCA H0RD /PUT IN H0RD
JMS TRFL0T /CHNG TO FLOATING PT
JMP 1 EFUN31 /DONE
TRBEG, -3 /STARTS DATA AT LOC 0
TRCURAD=0010
TRFL0T, 0 /CHNG 2WORD INT TO FLT PT
DCA EXP \/*CLEAR EXP*  
TAD HORD  
SZA CLA  
JMP TR2F \/*HORD NOT 0*  
TAD L3RD  
SNA CLA  
JMP I TRFLJT \/*NUMBER=0*  
TR2F,  
  CLO RAL \/*BEGIN SHIFT*  
  DCA L3RD \/*PUT BACK FOR NEW*  
  TAD HORD \/*GET HORD W3RD*  
  RAL \/*ROTATE, LINK IN*  
  S3L \/*DONE ROTATING IF L=1*  
  JMP TR2FL \/*FINISH*  
DCA HORD \/*PUT BACK L3RD*  
ISZ EXP \/*WILL NEVER BE 0*  
JMP TR2F  
TR2FL,  
  JMS TR2FLA \/*WHICH ROTATES RIGHT*  
  TAD HORD \/*READY FOR ANOTHER*  
  JMS TR2FLA  
  TAD EXP \/*GET EXP*  
CIA  
  TAD TR24 \/*ADD 24 DEC*  
DCA EXP \/*THE REAL EXP*  
JMP I TRFLJT \/*RETURN*  
TR24,  
  0030 \/*24 DECIMAL*  
TR2FLA,  
  RAR  
  DCA HORD \/*PUT IT BACK*  
  TAD L3RD \/*PICK UP L3RD*  
  RAR \/*ROTATE LINK IN*  
  DCA L3RD  
  JMP I TR2FLA \/*RETURN*  
FTRADD,  
  0  
  INT \/*CELL 0 AND INT*  
  CLO RAL \/*MUL BY 2*  
  TAD TRBEG \/*ADD OFFSET*  
  JMP I FTRADD \/*RETURN*  
FTR4,  
  INT \/*GET DATUM*  
  6377 \/*GIVE, RECEIVE DATA*  
  DCA L3RD \/*LD INT3 L3RD*  
  DCA HORD \/*FAKE LIKE ITS 2W3RD INT*  
  JMS TRFLJT  
  JMP I EFUN31 \/*DONE*  
FTR5,  
  6373 \/*START DATAJUT*  
  INT  
  CIA \/*FORM -# OF CELLS*  
  DCA TRCNTR \/*COUNTER*  
  PUSHJ  
  EVAL-1  
  JMS FTRADD \/*GET CELL ADD*  
  DCA TRCURAD \/*CURRENT ADD*
TAD TRCURAD
DCA TRCUR2 /FORM IDENTICAL PNTR
TAD TRDOUT
6375 /SET UP DAT3OUT
CLA CLL /CLEAR
CDFI
TRCUR2=0011
TRCNTR=0004

FTR5A, 6376 /GET A DATUM
TAD I TRCURAD /ADD TO CUR LORD
DCA I TRCUR2 /REPLACE IT
TAD I TRCURAD /GET LORD
SZL /DONT INC UNLESS JFL3
IAC CLL /ADD ONE TO LORD
DCA I TRCUR2 /REPLACE LORD
6371
JMP *-1 /TREAD WATER TILL READY
ISZ TRCNTR /DON'T YET?
JMP FTR5A /N3
CDF0 /YES
TAD TRDT2
6373 /TURN OFF DAT3OUT
JMP I EFUN31 /FINISH

TRDOUT, 4000 /COM FOR DATA
TRDAT30M, 3420 /DAT3OUT START
TRD23, 3401 /DAT3OUT STOP

FTR2, JMS FTRADD /GET ADDRESS OF CELL
DCA TRCURAD /LOAD IT
PUSHJ
EVAL -1 /GET Y
JMS TRINT /CHNG TO 2W3RD INT
CDFI
DCA I TRCURAD /LD LORD
CDF0
TAD LORD
CDFI
DCA I TRCURAD /LD LORD
CDF0
JMP I EFUN31 /DONE

TRINT, 0 /FLT PT TO 2D INT
CLA
TAD LORD
RTL /FIND A I?
SNL /CHECK FOR I5
JMP I TRINT /#=0
CLA
TAD EXP
TAD TR23 /ADD -23 DEC
SNA
JMP I TRINT /N3 SHIFT CASE
DCA EXP

TRINTI, TAD LORD
CLL RAR /START SHIFT
DCA      HØRD
TAD      LØRD
RAR      /RØT L IN
DCA      LØRD
ISZ      EXP      /DONE YET?
JMP      TRINT
TAD      LØRD
JMP I    TRINT
TR23,    7751     /=-23 DECIMAL

PEAK AVG-

C-FØKAL, 1977

01.01 C AVG PULSE HEIGHTS FROM T.R.
01.10 S C=0; S H=0; A "@ PULSES"; N;" MIN HEIGHT "M
01.20 I 1=200, 300; S Z=FCØM(2,1,0)
01.30 I (144-FCØM(4,1792))1.3,1.5,1.3
01.50 S Z=FCØM(5,400,1) JD 3:1 (C-N)1.2
01.60 T "MAX = "H" AFTER "C" PULSES; H/C = "H/C
01.70 Q

03.10 S Z=0; F I=250, 300; I (Z-FCØM(1,1))3.25,3.15,3.15
03.15 C SHITMØUSE
03.20 S Z=Z-FCØM(1,201); I (Z-M)3.22; S H=H+Z; S C=C+1
03.22 R
03.30 S Z=FCØM(1,1)

01.10 S Z=FNEW(2); S Z=FNEW(3,40); W AIT "*"; I
31.20 S Z=FNEW(3,200); S Z=FNEW(1)
OUTPUT.BAS
1 REM -- OUTPUT - TEXT SPITTER FOR ALLIGNING LP: PAPER
2 REM 14 MAR 80 BY C REISER
10 PRINT 'Source file'; \ INPUT S$
20 OPEN S$ FOR INPUT AS FILE #1
30 OPEN 'LP:' FOR OUTPUT AS FILE #2
40 LX=0\ PX=1%
50 IF END #1 THEN CLOSE #1,\#2 \ STOP
60 LINPUT #1,L$ \ LX=LX+1%
70 PRINT #2,L$
80 IF LX=66\ THEN LX=0\ \ PX=PX+1%
85 IF PX=2\ THEN PX=1\ \ GOSUB 95
90 GO TO 50
95 CLOSE #2 \ OPEN 'LP:' FOR OUTPUT AS FILE #2
96 PRINT 'OK for more'; \ INPUT A$ \ RETURN
100 END

RUNCDM.TXT
.PS 60
.SP 2
.UC
.NJ
.LM 13
.RM 75
.ND
.NNNM
.TS 21 29 37 45 53 61 69 77
Appendix H. Consideration of some aspects of the SF$_6$ Hamiltonian

In this appendix we will consider tensor terms in the SF$_6$ vibration-rotation Hamiltonian which are capable of mixing clusters. If such mixing exists, intensity of strongly pumped transitions may be borrowed by clusters mixed to them, giving rise to anomalously large DR signals. These considerations have been provided by Dr. Harold W. Galbraith of the Los Alamos Scientific Laboratory.

H.1 Hyperfine interactions

Although the resolution of our experiment was not sufficient to resolve individual symmetry components of a cluster, the splittings within a cluster and between clusters in the ground vibrational state can be calculated [H-1]. Specifically, the matrix elements for the inter-cluster splitting in the ground state is given by

\[
T_{044}(J,J)_{\alpha\alpha} = (2^3 J_3^3 5)^{1/2}(2J+1) \| T_{\nu}(0) \| \| T_{J}(4) \| \begin{bmatrix} 1 & 1 & 0 \\ J & J & 4 \\ J & J & 4 \end{bmatrix}
\]

\[
\times (-1)^J F_{A_1\alpha\alpha}^{(4JJ)} c_{044}
\]

\[
= (-1)^J F_{A_1\alpha\alpha}^{(4JJ)} \sqrt{\frac{3}{28}} \{ (2J-3)(2J-2)(2J-1)2J(2J+1)
\]

\[
\times (2J+2)(2J+3)(2J+4)(2J+5) \}^{1/2} c_{044}
\]

(H-1)
Recently Borde et al. \cite{H-2} have estimated that $^{0}T_{044} = 6$ Hz from very high resolution saturation spectroscopy. Using this value, calculation of $(H-2)$ for $J = 33$ renders
\[ T_{044}(JJ)_{\alpha\alpha} = -\frac{F_{(4,33,33)}}{A_{1\alpha\alpha}} \times 322 \text{ MHz} \]  
(H-3)
Using the expressions of Krohn \cite{H-1b} for the $F^4$ coefficients in (H-3), the ground state cluster spacing is approximately 5.7 MHz for 4-fold axis clusters and 4.8 MHz for 3-fold axis clusters.

As Borde et al. point out \cite{H-2}, symmetry states within a cluster are mixed by spin-rotation and spin-spin interactions. Spectroscopically, they have shown mixing of the $E^{0}$ and $F^{0}$ states of $Q(36)$ as "crossover peaks" occurring between the $E^{0}$ and $F^{0}$ peaks. These transitions violate the $\Delta C = 0$ selection rule by virtue of tensor spin-spin interactions which are off-diagonal in the cluster approximation. The crossover peak intensities, which are proportional to the square of the mixing, are at best 10%.

The ground state splitting between these two symmetry components can be calculated from (H-3) to be $\sim 4$ kHz. Since, in our case, the intercluster splitting is about 5 MHz, the intercluster mixing will be down by a factor of 10$^3$. Hence hyperfine interactions are far too weak to perturb DR intensities between clusters, and may be eliminated as a mechanism for transferring intensity.

H.2 Centrifugal distortion
The only other ground state molecular mixing process to be considered is due to the sixth rank tensor centrifugal distortion operator, given for 4-fold axis clusters by

\[ g = 0_{t_{044}} \frac{1}{8} \left[ V_0^6 - \left( \frac{7}{2} \right)^2 (V_4^6 + V_{-4}^6) \right] \]  

(H-4)

This operator mixes states of \( \Delta K = 0, \pm 4 \) (and \( \Delta K = 0, \pm 3 \) for 3-fold axis clusters). Evaluation of this expression provides, for \( J = 33 \),

\[ g = 0_{t_{066}} \frac{14 \cdot 4}{64} \frac{1}{11 \cdot 9} (2J+1)^{-1}(2J+7)(2J+6)\cdots(2J-5) \frac{1/2}{1/2} \begin{pmatrix} J & 6 & J \\ 27 & 4 & -31 \end{pmatrix} \]  

(H-5)

\[ = 1.3 \times 10^8 \ 0_{t_{066}} \]  

(H-6)

for \( 0_{t_{066}} \) expressed in Hz.

In the 2-level experiment, the sixth-rank tensor interaction couples the \( F_1^5 + F_2^4, K = 27 \) cluster, which is nearly resonant with the pump field, with the \( F_1^2 + F_2^1, K = 31 \) cluster. Evaluating the appropriate \( F^4 \) coefficients to find the splitting between these two clusters in the ground state, we find via (H-3) that this splitting \( \delta \) is

\[ \delta = (3.5 - (-1.8)) \times 10^{-2} = 322 \text{ MHz} \]  

\[ = 17 \text{ MHz} \]  

(H-7)

This is the energy difference over which the perturbation interaction of (H-6) must apply. The extent of mixing is
given, in a simple perturbative approach, by

\[
\text{mixing} = \frac{g}{\delta} = \frac{1.3 \times 10^8 \, o_t^{066}}{1.7 \times 10^7} = 7.6 \, o_t^{066}
\]  

Hence, for 10% mixing we require that \( o_t^{066} > 10^{-2} \) Hz.

Although a measurement of \( o_t^{066} \) has not been made, its size can be obtained by standard vibration-rotation ordering.

We assert that

\[
\frac{o_t^{224}}{B} = \frac{o_t^{066}}{o_t^{044}} \tag{H-9}
\]

where \( B \) is the rotation constant, since both ratios are taken between parameters which differ by two orders in \( J \). Using best values [H-3] for the known constants in (H-9), we find that

\[
o_t^{066} = \frac{o_t^{044} o_t^{224}}{B} = \frac{6 \times 3.8 \times 10^{-5}}{10^{-1}} \tag{H-10}
\]

\[
= 2 \times 10^{-3} \text{ Hz}
\]

We conclude that although this is a possible source of mixing, it would take an unusually large molecular constant \( o_t^{066} \) to give appreciable mixing of ground state clusters and hence is unlikely.

\[H.3 \ "Weak" \ transitions\]

In the excited vibrational state mixings must occur over
even larger detunings than for ground state misings. The primary such mixing is due to the second order Coriolis tensor \( \mathcal{C}_{224} \), which mixes different \( R \) (pure rotation) values of the same \( J \). This mixing leads to the "weak transitions" of Galbraith et. al. [H-43], which have been suggested [H-5] to be important in the multiphoton absorption process. According to [H-4], weak transitions to the same upper state belong to lower states having different \( J \) values. The energy difference \( \delta \) between the ground states can be simply estimated by

\[
\delta = B_0 J(J+1) - B_0 (J+1)(J+2) = 6 \text{ cm}^{-1} \text{ (H-11)}
\]

The very large size of \( \delta \) in this case indicates that mixings of this type would not be observable in this experiment.

H.4 Optical mixing

The final class of possible mixings are optical, or molecule-pump field coupling. We will consider only dipolar and ignore higher n-pole and magnetic interactions.

In the standard treatment [H-6] the molecular dipole is expanded in normal coordinates in a Taylor's series. In the lab frame it is a permutationally invariant vector, and hence is a double tensor of indices \((1,A_{lg})\). The molecule-fixed components are related to the laboratory-fixed components by a \( D^{(1,1)} \) rotation matrix. We can write [H-7]

\[
\mu \text{ }_{\text{LAB}}(1,A_{lg}) = \langle D^{(1,1)} \rangle \times (\mu_0 q_3(0,1) + \{q_3 x q_3 x q_3\}(0,1) \mu_2^a \\
+ \{q_3 x q_3 x q_3\}(0,3) \mu_3^b + \ldots \rangle(1,A_{lg}) \text{ (H-12)}
\]
From (H-12) two kinds of terms arise, $T_{110}$ and $T_{314}$, which are scalars and fourth rank tensors of $A_{1g}$ symmetry, respectively. Since the $T_{314}$ tensor has a vibrational rank of 3 it cannot connect 0 $\nu_3$ states with 1 $\nu_3$ states, hence no mixing via this operator occurs. Furthermore, $T_{110}$ is a scalar in $R$ and cannot mix clusters to any order. Hence, mixing by optical dipole interactions can be ruled out also, leaving no terms in the dressed molecular Hamiltonian which appreciably mix clusters in a given $J$ level.
Appendix I. Gizmos

I.1 TAC II CO₂ TEA laser

Aligning the optical cavity of the TAC II laser follows a procedure similar to that used for aligning other infrared lasers in the laboratory. The output coupler must be removed by unbolting its gimbal mount and removing the entire mount. Next, the brewster angle ZnSe windows must be replaced by pinholes machined into round aluminum stock, made specially for this job. A HeNe laser can then be directed by means of a micrometer-mounted mirror through the two pinholes. The beam should strike the grating in the center.

Alignment of the grating can be checked by turning the “tuning” micrometer handle to insure that successive diffraction orders of the HeNe beam fold back into the pinholes. The vertical tilt micrometer can be tweaked accordingly. Once the HeNe beam and grating are aligned, the windows and output coupler can be replaced. The output coupler is then adjusted until the reflection of the HeNe beam from the outside surface of the coupler folds back into the HeNe laser itself. In this manner one is assured that the output coupler is perpendicular to the optical axis of the TEA laser cavity.

Final tweaking of the grating may be tedious. The best chance for lasing occurs when the front surface of the grating...
is parallel to the back plate of its gimbal mount. When the laser is finally turned on, the grating must be slowly tuned until lasing occurs on some random line. The front mirror can then be tweaked. The calibration of the tuning thumbscrew on the grating can be checked against the CO₂ laser spectrum analyzer. Adjustment of the tuning calibration can be done by temporarily loosening the set screws on the tuning micrometer sleeve, turning the outside thumbscrew to the desired digit while holding the micrometer handles still, then tightening the sleeve set screws.

The calibration of the Optical Engineering CO₂ laser spectrum analyzer can also be checked with a HeNe laser. By shining the HeNe directly into the analyzer, three diffraction orders should be visible on the analyzer screen. The middle spot, the sixteenth order spot, is very nearly coincident with the R(48) 10.6 micron laser line; the calibrated screen can be adjusted accordingly.

I.2 N₂O laser secrets

Much useful information on the operation of the Q-switched N₂O laser was found in Joel Levy’s research notebooks. The comments below may also be of use in its operation.

1) The 1.5 cm bore Q-switched CO₂ laser will not lase with N₂O presumably because of the large bore (poor cooling) and long residence time of the gas in the tube.
2) In the N\textsubscript{2}O laser, discharge is difficult to sustain with no CO (carbon monoxide) in the mixture. CO turns the discharge blue. The three lead power supply having 100 K resistive ballasts in the high voltage leads is necessary to maintain discharge in both arms of the tube.

3) The N\textsubscript{2}O laser lases well using CO\textsubscript{2} as a gain medium. Thus CO\textsubscript{2} can be used to align the optics with ease, then replaced with N\textsubscript{2}O.

4) Best lasing with N\textsubscript{2}O was had with a mixture of N\textsubscript{2}O:CO:N\textsubscript{2}:He of 1:0.5:1:3.5 Torr, with minimum current necessary to sustain discharge. It was necessary to reduce the total pressure in the tube to below one Torr to ignite the discharge, after which the pressure was increased slowly to an operating pressure of about 6 Torr.

5) Q-switched lasing is impossible in the 1 cm bore tube with a 10 or 20 meter radius mirror. Q-switched lasing was obtained using a flat mirror at one end, and a rotating 20 meter radius mirror and a 4.25 m radius stationary mirror at the other end. The current configuration utilizes a 4.5 meter radius rotating mirror and a plane grating.

6) Maximum repetition rate for the N\textsubscript{2}O laser is about 58 Hz. Care must be taken to avoid frequencies close to line current, lest the beat note between the laser repetition frequency and line frequency be detected by sophisticated electronics.
I.3 Boxcar settings for DILDOR

Typical settings of the PAR Model 160 boxcar integrator for DILDOR experiments are as follows (\( ? \) means does not matter):

- Trig mode — EXT
- O.T.D. — \( ? \)
- Slope — negative
- Threshhold — as needed
- D.O. — DELAY
- Repeat — \( ? \)
- Input — 100K
- Prefilter — 0.005 MHz
- Coupling — AC
- In. sens. — 50 mV
- Time base — 0.1 msec
- S/D — as needed
- Scan rate — 1 min
- Blue TC — \( ? \)
- Ap. Time — 0.1 sec, min dial
- Red TC — 0.1 msec
- Zero — as needed
- Memory — OFF
- In. offset — OFF
- Throshhold — as needed
- Throshhold — DELAY
- Ap. Time — 0.1 sec, min dial
- Throshhold — as needed
- DELAY
- Ap. Time — 0.1 sec, min dial
- Throshhold — as needed
- DELAY
- Ap. Time — 0.1 sec, min dial
- Throshhold — as needed
- DELAY

I.4 PDP-8/L to MINC link

Characters can be transferred from the PDP-8/L to the MINC with the cable diagramed in Fig. I-1. This cable plugs into an SLU port on the MINC. To effect transfer, output from the 8/L is transferred to the ARDS by executing an FNEW(S) function. A program such as PDPBIN (listed below) must be running on the MINC. This program accepts any characters typed on the ARDS, line by line, as input and stores them on diskettes. In this fashion a FOCAL program can write data on the ARDS and effect data transfer; FOCAL programs can be transferred with a WRITE ALL command.

With a minor modification to the FOCAL operating system, the PDP-8/L can be used as a paper tape reader for the MINC. In this mode, a tape is not read into 8/L memory, but is merely transferred to the MINC as it is read. The instructions
Fig. I-1. PDP-8/L to MINC link. A three conductor ribbon cable was connected to the existing board in the 8/L which is used for communication to the ARDS.
1. Load FOCAL
2. Execute FNEW(5) so that output goes to ARDS
3. RUN PDPBIN on MINC
4. STOP the 8/L
5. Load these two locations with instructions:

<table>
<thead>
<tr>
<th>location</th>
<th>instruction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2030</td>
<td>4355 READC = JMS 2155</td>
</tr>
<tr>
<td>2031</td>
<td>5230 JMP .-1</td>
</tr>
</tbody>
</table>
6. Place tape in LSR
7. Start 8/L at location 2030
8. Start LSR
9. That's all

When the entire tape is read, stop the LSR. PDPBIN can be stopped with two CTRL/C's.

PDP8IN.BAS

```
1 REM -- stop program with "C" then type 'CLOSE #1'
4 PRINT "Filename for data"; INPUT F$
5 OPEN F$ FOR OUTPUT AS FILE #1
10 CIN('retrieve',S$)
20 IF ASC(SEG$(S$,1,1))=138 THEN S$=SEG$(S$,2,100)
30 PRINT #1,S$ \ GO TO 10
50 OPEN F# FOR INPUT AS FILE #1
60 FOR I=1 TO 3 \ INPUT #1,S$ \ PRINT S$ \ NEXT I
70 CLOSE #1
:00 END
```

1.5 TEA laser pulse counter

A small digital pulse counter was built in 1977. The wiring for this counter is shown in Fig. I-2. Separate switches control power, reset and count direction (up/down).
Fig. I-2. Circuit diagram for TAC II pulse counter.
Connection is made by simple BNC cable to the SYNC OUT connector on the TAC II laser, although the counter may work in other applications as well.
APPENDIX J. Laboratory Report: Studies of SiH₄ using CO₂ lasers

In 1978, J. Haggerty and R. Cannon (and coworkers) discovered that sinterable powders of silicon nitride (Si₃N₄) could be produced in an atmospheric pressure flow of silane and ammonia when irradiated with approximately 100 W/cm² of c.w. CO₂ laser radiation [1.2]. Many details of the process were unknown, such as the detailed gas phase chemical mechanisms, absorption cross sections as a function of temperature and pressure, the possibility of multiple photon absorption, etc. A collaboration between that Energy Laboratory group and Prof. Steinfeld's group was initiated with the hopes of investigating the possibility of multiple photon heating of silane and silane/ammonia mixtures, and of obtaining accurate values of the absorption coefficients of those gases for the various CO₂ laser frequencies. The absorption coefficients were needed for modeling the energy deposition in the c.w. experiments, and to ascertain which laser line would be most efficient in heating the mixtures. It was hoped that multiple photon induced dissociation of silane would help to unravel the complex gas phase chemical mechanisms by which the powders were formed, but these experiments proved to be disappointing. This Appendix was submitted to Haggerty and Cannon at the conclusion of several months of work, and is contained in their final program report, Reference 1.2.
Experimental

Two types of experiments were performed: low pressure, high intensity irradiation with a pulsed CO₂ laser, and simple measurement of the attenuation of c.w. CO₂ laser lines. In both sets of experiments, silane was used from the tank after many freeze-pump-thaw cycles; NH₃ was treated similarly. Cl₂ used in one experiment was obtained from an ultra high purity lecture bottle.

Typical pulses from the Tachisto Model 215G CO₂ TEA laser contain 0.3J with a FWHM of about 50 ns. Usually 500 pulses were used for each sample at a rate of 1 Hz. Figure 1 shows the apparatus used for the irradiation; joulemeters (9 and 11 in diagram) allow the percent transmittance of the sample to be measured to ± 5%. Two lenses were employed to vary the focal geometry of the beam and thereby to control the peak fluences at the focal point of the beam. For an effective focal length for the telescope of 67 cm, the beam radius at the focus is 0.66 mm; with .3J/pulse, the fluence at the focus would be 22 J/cm². Similarly, with a focal length of 28 cm, the fluence would be increased to 1.5 x 10³ J/cm². In this manner the peak fluence could be adjusted from a relatively weak value to the point where dielectric breakdown occurred in the sample.

Reagent pressures were read from an MKS 2000A pressure transducer with a 0.1-1000 torr stated range although the head was found to be sensitive to 10⁻² torr. The response of the transducer was checked against a dibutylphthalate manometer. Mixtures of gases were prepared by successively freezing known quantities of gas into a cold finger in the cell. After irradiation, the products were characterized by their
infrared spectrum, taken on a Perkin-Elmer 567 IR spectrophotometer. A variety of laser lines, sample pressures, and sample mixtures were investigated, as can be seen in Table II.

Two methods were used to obtain the absorption coefficients of SiH₄ and NH₃, differing slightly in technique as dictated by the availability of equipment. The apparatus in Figure 32a was employed for all but a few data points; it employs two choppers to modulate the sample and reference beams at different frequencies, allowing two lock-ins to detect the sample and reference intensities independently while using the same detector. When only one chopper was available, it was positioned to modulate the two beams at a relative phase of 90°, again allowing independent measurement with one detector.

The laser itself consists of a 1m gain cell with a rotatable grating and a 5m radius mirror forming the cavity; the beam emerges via a small hole in the mirror, which is mounted on a piezoelectric crystal. The stabilization network depicted in Figure 33 minimizes output intensity drift caused by thermal expansion of the aluminum girder supporting the optical elements. By modulating the mirror position by +0.5 micrometers, the frequency of the cavity resonance is modulated under the CO₂ gain curve. A lock-in detects the slope of the gain curve at the cavity mode frequency by demodulating the very slight ripple in the laser output and applies an error voltage to the pzt to bring the cavity mode to the peak of the gain profile.

Two cells were employed with 1.73 cm and 9.97 cm lengths fitted with perpendicular NaCl windows. When possible, sample pressures of about 130 torr were used; for very strongly attenuated lines, it was necessary to employ lower pressures. Again, the MKS 2000A pressure
Fig. 31. Apparatus for TEA laser experiments. 1. Tachisto Model 215G laser; 2,6. irises; 3. attenuation cell; 4. beamsplitter; 5,7. telescope lenses; 8. sample cell with pressure head; 9,11. joulemeters; 10. inverting differential amplifier; 12. signal alternater; 13. Blomation digital scope.
Fig. 32. Apparatus for absorption measurements. 

a) two chopper method. 
1 - laser; 2,3,6,7 - mirrors; 4,10 - ZnSe beamsplitters; 5,8 - choppers; 9 - sample cell; 11 - pyroelectric detector; 12 - reference channel lock-in; 13 - sample channel lock-in; 14 - PDP 8/L computer. 

b) single chopper method; 
lockin 13 is set to 90° relative phase.
Fig. 73. Stabilized CO₂ laser used in absorption measurements. 1 - rotatable grating; 2 - detector; 3 - Im gain tube; 4 - pzt mounted mirror; 5 - lock-in; 6 - manual dc offset; 7 - high voltage op amp. Depiction of cavity resonances under a Doppler-broadened gain profile is shown at right.
head was used after calibration against a mercury manometer.

The procedure for measuring the attenuation of a sample is straightforward. The laser was tuned to the desired line, and the stabilization network activated. With the sample frozen into a cold finger in the cell, the ratio of the sample and reference lockin's signals was averaged for approximately one minute (about 400 samples) by a PDP 8/L computer. The sample was then thawed and the ratio again averaged for one minute. The laser was then tuned to the next line, etc. The transmittance, \( T \), is given by

\[
T = \frac{I/I_0 \text{ (sample unfrozen)}}{I/I_0 \text{ (sample frozen)}} \tag{J-1}
\]

where \( I \) and \( I_0 \) are actually the voltages from the sample and reference lock-ins respectively. Typically the 67\% confidence limits of \( T \) were \( \pm 3\% \). The extinction coefficient \( \alpha \) can be calculated from \( T \) and the known sample pressure \( p \) and cell length \( l \) via

\[
\alpha = \frac{1}{pl} \ln T \tag{J-2}
\]

All measurements were taken at room temperature. During the course of a measurement the samples did not absorb enough power to raise the temperature of the cell noticeably.

**Results**

Table J1 contains a summary of results for the TEA laser experiments. No reaction was noted for conditions which did not produce dielectric breakdown inside the cell, which is evidenced by a blue-white spark. The
breakdown threshold is sensitive to sample pressure and peak intensity; for silane pressures above 2 torr, breakdown always occurred for fluences of $1.5 \times 10^3$ J/cm². For fluences below 100 J/cm², however, breakdown did not occur for pressures up to approximately 5 torr. For conditions where no breakdown occurred, no incondensible gas (i.e. H₂) was observed in the cell after irradiation and no change in the reagent IR spectrum occurred. One attempt was made to trap any H₂ which may be produced by adding CI₂; even a mixture of one torr each was sufficient to cause breakdown using the 28 cm focal length optics. Lower pressures in this case would produce quantities of products too small to detect with our apparatus, hence this experiment was abandoned.

Several attempts were made to induce reaction in mixtures of silane and ammonia. These experiments were marked by difficulty similar to the silane-only experiments. For a given pressure of gas a long focal length produced no reaction but a short focal length caused breakdown.

Table 2 exhibits the extinction coefficients $\alpha$ for NH₃ and SiH₄ for laser lines in the 10.6 micrometer CO₂ laser band. Good agreement with the results of Patty et al. (Appl. Opt. 13, 2850 (1974)) is seen for the ammonia absorptions. For very strong attenuations, it was necessary to decrease the sample pressure; values for $\alpha$ are noted in parentheses where the uncertainty in $I/I_0$ (with sample) exceeded 25%, due to the opacity of the gas at the particular laser line.

Discussion

Failure of the TEA laser experiments is disappointing. Since pyrolysis of silane can be accomplished with long pulses or c.w. radiation at a few tenths of an atmosphere, we know that a dissociation channel is available to sufficiently hot molecules. Apparently for these
<table>
<thead>
<tr>
<th>Silane only:</th>
<th>line</th>
<th>p(torr)</th>
<th>lens f.l. (cm)</th>
<th># of shots</th>
<th>results</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(20)</td>
<td>4.6</td>
<td>80</td>
<td>2000</td>
<td>no change in p or spectrum; no powder</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.21</td>
<td>28</td>
<td>2200</td>
<td>slight brown powder</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.4</td>
<td>28</td>
<td>400</td>
<td>heavy powder; p increase; breakdown</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>28</td>
<td>500</td>
<td>light powder; p increase</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>66</td>
<td>1000</td>
<td>no changes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>28</td>
<td>1500</td>
<td>breakdown on first pulses</td>
<td></td>
</tr>
<tr>
<td>P(24)</td>
<td>2.0</td>
<td>28</td>
<td>2200</td>
<td>slight powder, p increase; breakdown</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.57</td>
<td>28</td>
<td>700</td>
<td>powder, breakdown</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.54</td>
<td>28</td>
<td>2000</td>
<td>no change</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1:1 torr Cl₂</td>
<td>28</td>
<td>1500</td>
<td>breakdown on first 250 shots</td>
<td></td>
</tr>
<tr>
<td>Silane/ammonia</td>
<td>0.6/1.2</td>
<td>67</td>
<td>2300</td>
<td>no changes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6/1.2</td>
<td>28</td>
<td>1000</td>
<td>no changes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.4/3.7</td>
<td>67</td>
<td>1000</td>
<td>no changes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.4/3.7</td>
<td>28</td>
<td>1000</td>
<td>breakdown; slight power, p increase</td>
<td></td>
</tr>
</tbody>
</table>
Table J2. Absorption coefficients (atm-cm)$^{-1}$ for the 10.6 $\mu$m band of the CO$_2$ laser. $a = -1/p_t \ln T$.

<table>
<thead>
<tr>
<th>(J)</th>
<th>NH$_3$ R</th>
<th>P</th>
<th>SIH$_4$ R</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>.044</td>
<td>1.02</td>
<td>1.68</td>
<td>1.05</td>
</tr>
<tr>
<td>36</td>
<td>.01 (not measured)</td>
<td>1.8</td>
<td>.27</td>
<td>18.1</td>
</tr>
<tr>
<td>34</td>
<td>.0072</td>
<td>3.5</td>
<td>(small)</td>
<td>5.01</td>
</tr>
<tr>
<td>32</td>
<td>.0065</td>
<td>13.6</td>
<td>.19</td>
<td>3.79</td>
</tr>
<tr>
<td>30</td>
<td>.047</td>
<td>.87</td>
<td>.96</td>
<td>6.46</td>
</tr>
<tr>
<td>28</td>
<td>.057</td>
<td>.35</td>
<td>2.68 (24.4)</td>
<td>8.94</td>
</tr>
<tr>
<td>26</td>
<td>.059</td>
<td>.42</td>
<td>.70</td>
<td>7.42</td>
</tr>
<tr>
<td>24</td>
<td>.056</td>
<td>.16</td>
<td>.31 (34.5)</td>
<td>10.7</td>
</tr>
<tr>
<td>22</td>
<td>.071</td>
<td>.13</td>
<td>1.36 (28.9)</td>
<td>8.17</td>
</tr>
<tr>
<td>20</td>
<td>.12</td>
<td>.22</td>
<td>.30</td>
<td>1.61 (43.0)</td>
</tr>
<tr>
<td>18</td>
<td>7.25</td>
<td>.18</td>
<td>.87</td>
<td>11.8</td>
</tr>
<tr>
<td>16</td>
<td>.24</td>
<td>.41</td>
<td>1.14</td>
<td>.96</td>
</tr>
<tr>
<td>14</td>
<td>.47</td>
<td>.50</td>
<td>.83</td>
<td>.79</td>
</tr>
<tr>
<td>12</td>
<td>21.5</td>
<td>.65</td>
<td>.23</td>
<td>3.95</td>
</tr>
<tr>
<td>10</td>
<td>.16</td>
<td>.34</td>
<td>.50</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>.35</td>
<td>.007</td>
<td>2.70</td>
<td></td>
</tr>
</tbody>
</table>

Conditions:

- **A**: 136 $\pm$ 2 torr 10 cm cell
- **B**: 130 $ \approx 1.7$
- **C**: 53 $\pm$ 1 $ \approx 1.7$; $a > 20$ untrustworthy
- **D**: 11 $ \approx 1.7$
- **E**: 25 $ \approx 1.7$ single chopper method
conditions, individual silane molecules do not absorb sufficient photons to overcome the dissociation reaction energy barrier. If we assume this barrier is the Si-H bond enthalpy (approx 70 kcal/mole) a molecule must absorb at least 26 photons with $\lambda = 10.6$ micrometers before dissociation could occur. Presumably silane molecules absorb on the average for fewer than 26 photons, even at the focal point of the beam.

The possibility of a multiple photon dissociation of silane cannot be precluded, however, for fluences much higher than those used here. To utilize fluences greater than $2 \times 10^3$ J/cm$^2$, sample pressures must be much below a torr. Our methods of analysis require more product than this would afford; typically these experiments are performed with an \textit{in situ} mass spectrometer. Also, production of powder at such low pressure seems implausible.

Agreement between the data of Patty et al. and this work is not surprising. Patty and co-workers prepared ammonia samples in parts-per-million concentrations in one atmosphere of air; one would expect a somewhat larger pressure broadening than for these conditions. This pressure broadening causes NH$_3$ absorption features to overlap the spectral bandwidth of the CO$_2$ laser employed; greater pressure or laser bandwidth will cause greater absorption. It should be noted that for neither Patty's measurements nor these is the laser bandwidth accurately known, although the lasers are of similar construction.

A dramatic effect on the absorptivities is seen for very strongly attenuated lines for both ammonia and silane: in all cases a decrease in $\alpha$ is observed for a decrease in pressure. Presumably this reflects the broadened nature of the individual absorption features, which are not in exact resonance with the laser lines until pressure broadening causes some spectral overlap between the molecular absorption and laser emission.
lineshapes. Since the exact positions of the absorption features, their relative intensities, and pressure-broadening parameters are not known for silane, it would be impossible to calculate the extinction coefficients for this molecule at a given pressure. If these parameters were known, the qualitative behavior of the absorption lines may be predicted for particular laser lines, but a more lucrative approach would be direct measurement of the attenuations at the pressures of interest.
BIOGRAPHICAL NOTE

Chris Reiser was born to Dr. Howard G. and Joanne E. Reiser at 10:17 P.M. on June 1, 1954, whereupon he was heard to say, "It was cooler in heaven." A life of academics was forecast for him at the age of seven, when his teacher at the St. Paul the Apostle Elementary School predicted that his handwriting would never be legible. Forsaking a career as a Latin linguist, he entered the arena of college science at the College of St. Francis in Joliet, IL, before graduating at the top of his class from Joliet Catholic High School in 1972. Shortly after matriculation into Lawrence University in Appleton, WI, he disappeared into Science Hall and is rumored to have lived from vending machine food alone until graduating magna cum laude in honors and in course in 1976 with a B.A. in chemistry-physics. Despite his shortcomings (he was a computer programmer), he was elected to Phi Beta Kappa.

Some say that Reiser's life really began in the fall of 1976 when he entered the Chemistry graduate program at MIT. His liveliness was recognized when he received the Graham S. Arnold Most-living-places-in-shortest-time Traveling Trophy, having had five separate addresses in a three year span. After dissertating under Jeff Steinfeld, he received his Ph.D. in chemical physics in the spring of 1980; his degree did not seem to improve his squash game, quarter-mile race time, or archery score. He maintains that the only academic award he has received is the American Legion Good Citizenship Medal for his outstanding performance as an eighth grader.